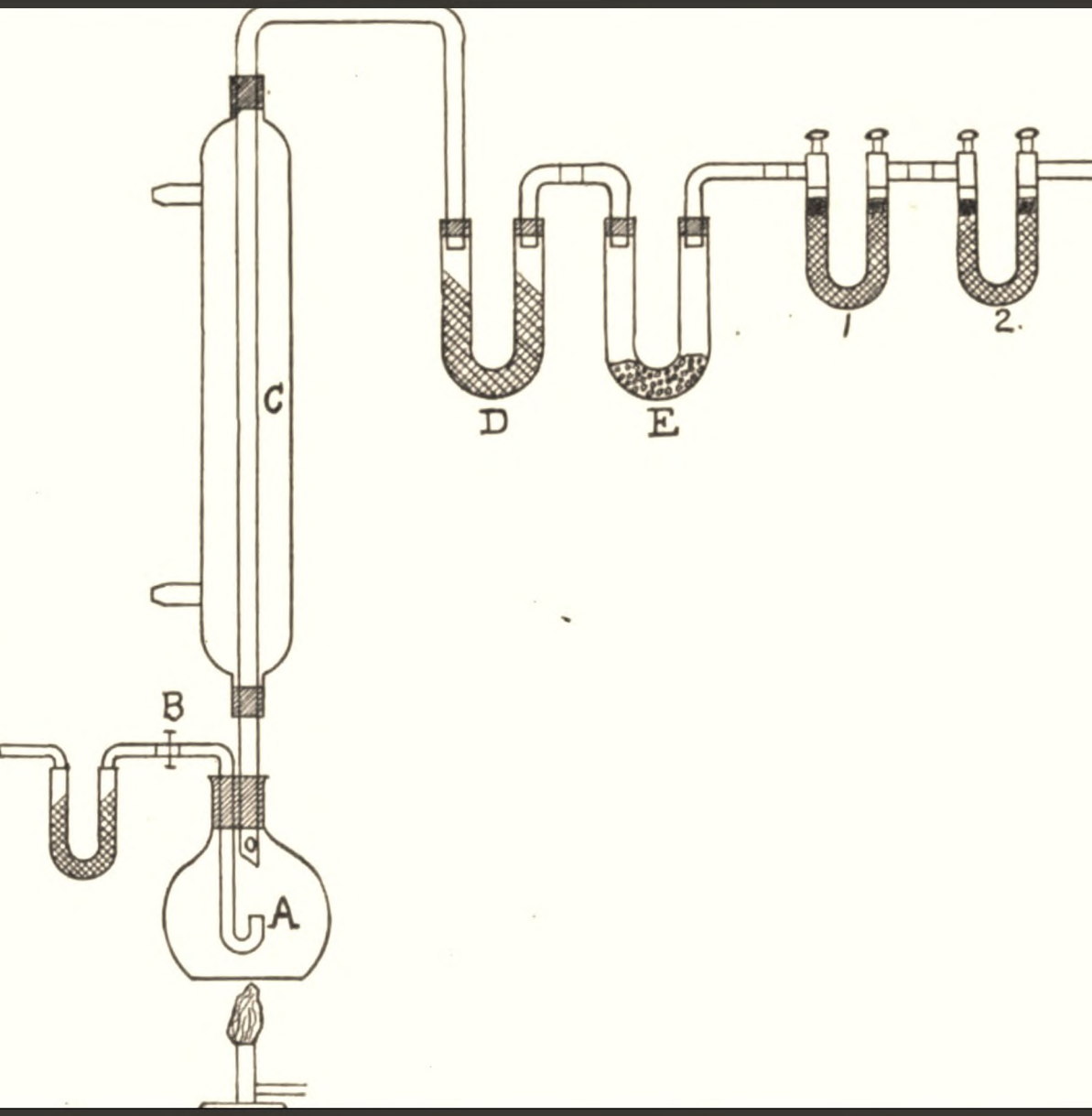


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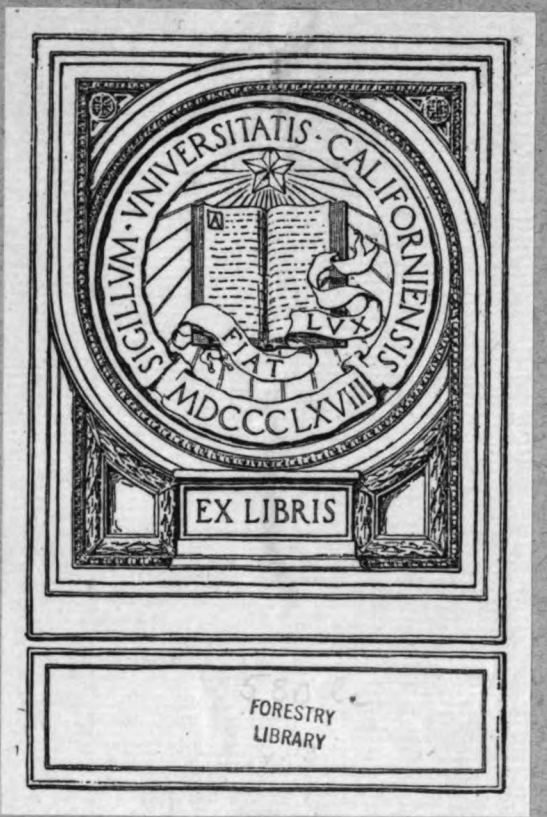


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Journal of the
# American Leather Chemists Association

Vol. III JANUARY, 1908 No. 1

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## SITUATIONS

By vote of the Council, the President is authorized to announce that he will use his best efforts, when desired, to bring together employers wishing leather chemists and leather chemists wishing situations.

Notices of situations offered or desired will be inserted in the Journal free of charge.

## OFFICIAL METHOD OF THE AMERICAN LEATHER CHEMISTS ASSOCIATION FOR TANNIN ANALYSIS

### *I. Crude Materials*

(1) *Moisture Determination*:

Upon receipt of the sample, grind promptly and dry 10 grams in the manner and for the period specified for evaporation and drying in extract analysis.

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(2) *Preparation of Sample for Extractions*:

Sample must be dried at a temperature not exceeding 60° C., and then ground to such a degree of fineness that the entire sample will pass through a sieve of 20 meshes to the inch (linear).

(3) *Amount of Sample and Proportion of Water for Extraction*:

For fresh materials the amount of sample and proportion of water for extraction should be such as to give between .35–.45 gram tannin per 100 cc. of solution. For spent materials this proportion should be approximated as closely as practicable.

(4) *Extraction of Sample*:

Extraction shall be conducted in a form of apparatus that permits the removal of the extractive solution from the influence of sustained high temperature, and shall be continued till a portion tested with gelatine salt solution fails to give a precipitate. At least 400 cc. of the first portions of extractive solution should be removed and not subjected to further heating. A thin layer of cotton must be used in order to prevent fine material passing over.

(5) *Analysis*:

After extraction and dilution, solutions must be heated to 80° C., and analysis conducted as per Official Methods for Extracts. In case of weaker dilutions than the Official Method specifies, the amount of hide powder must be reduced in proportion to the reduction of tannin.

Ten grams of the air-dried sample should be dried as in (1) to determine moisture content of the portion extracted and the analysis calculated and reported upon a "dry" basis. The tannin in fresh materials should also be reported on the basis of the moisture content of the sample "as received."

## *II. Analysis of Extracts*

(6) *Amount and Dilution for Analysis*:

Fluid extracts must be allowed to come to room temperature and weighed in stoppered weighing bottle. Such quantity shall be taken as will give from .35–.45 gram tannin per 100 cc. of solution, dissolve in exactly 900 cc. of distilled water at 80° C., and make up to mark after standing not more than 20 hours, nor less than 12 hours. Temperature must not go below 20° C.

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(7) *Total Solids*:

Thoroughly mix solution, pipette 100 cc. into tared dish, evaporate and dry as directed under "Evaporation and Drying."

(8) *Soluble Solids*:

To 1 gram of kaolin in a beaker add 75 cc. of solution; stir and pour on a 590 S. & S. 15 cm. plaited filter paper; return filtrate to paper for one hour, keeping filter full. At the end of an hour pour solution from filter or remove with pipette. Bring 800 cc. of solution to 20° C.; refill the filter with this solution and begin to collect filtrate for evaporating and drying so soon as filtrate comes clear. Keep filter full. Evaporate and dry the first 100 cc. of filtrate, as per "Evaporation and Drying."

Funnels and receiving vessels must be kept covered during collection of filtrate for evaporation.

(9) *Non-tannins*:

A quantity of hide powder sufficient for the number of analyses to be made shall be prepared in the following manner: Digest with twenty-five times its weight of water till thoroughly soaked. Add 3 per cent. of chrome alum in solution. Agitate by either shaking or stirring occasionally for several hours and let stand over night. Wash by squeezing through linen, continuing the washing until the wash water gives no precipitate with barium chloride. Squeeze the hide, using a press, if necessary, so that the wet hide will contain between 70 and 75 per cent. of water. Use approximately 20 grams of wet hide for moisture determination. Add to 200 cc. of the original solution such quantity of the wet hide as represents from 12 to 13 grams dry hide. Shake for ten minutes in some form of mechanical shaker and squeeze immediately through linen. Add 2 grams kaolin to the filtrate, stir and filter through folded filter (No. 1F Swedish, recommended) of size sufficient to hold entire filtrate, returning till clear. Evaporate 100 cc. of the filtrate. The weight of the residue must be corrected for the dilution caused by the water contained in the wet hide powder.

NOTE.—In order to limit the amount of dried hide powder used, determine the moisture in the air-dried powder and calculate the quantity equal to 12½ grams of actual dry hide powder. Take any multiple of this quantity according to the number of analyses to be made, and after chroming and washing as directed, squeeze to a weight representing 70% to 75% water. Weigh

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the whole amount and divide by the multiple of the 12½ grams of actual dry hide powder taken to obtain the weight of wet hide powder for 200 cc. of solution.

The non-tannin filtrate must not give a precipitate with a 1 per cent. gelatine 10 per cent. salt solution.

(10) *Tannin:*

The tannin content is shown by the difference between the soluble solids and the corrected non-tannin.

### *III. Analysis of Liquors*

(11) *Dilution*:

Liquors must be diluted for analysis so as to give as nearly as possible .7 gram solids per 100 cc. of solution.

(12) *Total Solids*:

To be determined as in Extract Analysis.

(13) *Soluble Solids*:

To be determined as in Extract Analysis.

(14) *Non-tannins:*

To be determined by shaking 200 cc. of solution with an amount of wet chromed hide powder, containing 70 per cent. to 75 per cent. moisture, corresponding to an amount of dry hide powder shown in the following table:

| Tannin range per 100 cc. | Dry hide powder per 200 cc. |
|---|---|
| .35——.45 gram. | 8——10 grams. |
| .25——.35 gram. | 5—— 8 grams. |
| .15——.25 gram. | 2—— 5 grams. |
| .00——.15 gram. | 0—— 2 grams. |

Solutions to be shaken for non-tannins as in Extract Analysis; 100 cc. must be evaporated as in Extract Analysis.

### *IV. Evaporation and Drying*

(15) *Evaporation and Temperature*:

All evaporations and dryings shall be conducted in the form of apparatus known as the "Combined Evaporator and Dryer," at a temperature not less than 98° C. The time for evaporation and drying shall be 16 hours.

(16) *Dishes*:

The dishes used for evaporation and drying of all residues shall be flat-bottomed glass dishes of not less than 2¾ inches diameter nor greater than 3 inches in diameter.

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*V. Determination of Total Acidity of Liquors*

(17) *Place 100 cc. of the liquor in a 500 cc. flask and make up to the mark with water.*

To 100 cc. of diluted liquor in a flask with tube condenser, add 2 grams of chemically pure animal charcoal. Heat to boiling temperature with frequent shaking, cool, filter and titrate an aliquot portion with decinormal alkali.

On public analytical work by members of this Association, the fact that the Official Method has been used, shall be so stated.

---

## PROVISIONAL METHODS FOR SAMPLING TANNING MATERIALS

(1) *Liquid Extract in Barrels*:

Samples to be taken at a temperature of 40° F. minimum from 10 per cent. of the packages, as near as possible, by means of sampling tube which shall enter the bung and extend to at least the center of the barrel. These samples to be thoroughly mixed, using due precautions to prevent evaporation, and a composite sample of at least 4 oz., in duplicate, removed, sealed and labeled, with date of sampling, name of material, invoice number, or other means of identification.

(2) *Liquid Extract in Bulk*:

Extract shall be thoroughly plunged and sampled by passing a sampling tube to the bottom, through at least five sectors of contents, samples to be mixed thoroughly and composite samples drawn, sealed and labeled as in liquid extract in barrels.

(3) *Liquid Extract in Tank Cars*:

*a.* Where tank car extract is unloaded without the use of direct steam, into an empty container, the method of sampling is to be the same as for liquid extract in bulk, the sample being taken from the container after the car is unloaded.

*b.* Tank cars unloaded without the use of direct steam shall be sampled by taking at least five pint samples of the extract as it flows from the car. One of these samples to be taken about 3 minutes after starting to unload, one to be taken about 3 minutes before unloading is completed, and other three samples to be taken at equal intervals between the first and last. These samples to be mixed and composite samples taken, sealed and labeled as usual.

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Or, in case direct steam is used in unloading a tank car, shipment may be sampled according to the methods of sampling the liquid extract in bulk, the samples being taken directly from the car.

(4) *Solid Extracts*:

Solid extracts shall be sampled by taking a section from the center of the package to the surface after the removal of the cover. Samples as taken shall be immediately placed in clean, dry, closed receptacles, and when sampling is completed, broken, thoroughly mixed and duplicate samples of at least 6 oz. placed in clean, dry, glass receptacles, sealed and properly labeled. Sampling at place of manufacture shall be conducted by running portion from middle of strike into a mold holding at least two pounds, and immediately after cooling, selecting samples for analysis by method given above.

On lots of 300 bags or 100 barrels or less, at least 5 per cent. of the bags or barrels shall be selected for sampling. On lots of 301 to 2,000 bags or 101 to 700 barrels, 3 per cent. shall be sampled. On lots of more than 2,000 bags or 700 barrels, 1 per cent. shall be sampled.

Where a considerable period of time elapses between the sampling and analysis of sample, the latter should be weighed on day of sampling, and certified weight should appear on label.

(5) *Crude Tanning Materials*:

Shipments in bags, mats or barrels, of barks, nuts, beans, fruits, leaves (ground and unground), roots and ground wood, are to be sampled by opening each of the packages chosen for sampling and selecting an equal portion therefrom. These samples to be mixed and composite samples of the required amount taken and labeled as usual. In lots of 20 tons or less, 5 per cent. of the packages shall be sampled. In lots of above 20 tons up to 101 tons, 3 per cent. shall be sampled. In lots of 101 tons or more, 1 per cent. of the packages shall be selected for sampling.

(6) *Crude Tanning Materials in Bulk*:

*a. Barks, Nuts, Beans, Pods, Ground Materials, etc.*

Equal portions shall be selected from at least five parts of the lot, mixed, sealed, and labeled in duplicate.

*b. Wood.*

Billets or logs shall be selected from at least five parts of the lot, and the sawdust obtained by sawing completely through each

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billet or log selected, thoroughly mixed, sealed and labeled in duplicate.

(7) *Sampling of Spent Tan and Spent Wood:*

Spent tan and wood samples should be taken from the top, middle and bottom of a spent leach, and placed in a covered pail, contents of pail to be stored in a covered barrel to be kept for the desired period. When laboratory sample is desired, thoroughly mix contents of the barrel and dry a portion over steam pipes in a location free from bark dust. The dry laboratory samples should be at least 10 oz.

(8) *Ground Barks and Cut Woods*:

These samples should be taken at intervals as the ground material enters the leach. Composite samples shall be made up from these samples and shall be submitted undried to the laboratory.

(9) *Liquor Samples*:

Routine samples shall be taken by plunging the liquor and removing a pint and storing in earthenware crocks, having earthenware lids. The samples should be of the same size and taken under exactly similar conditions. The storage of crocks should be located where the temperature averages between 40° and 70° F. For the laboratory sample plunge the crocks well and fill a pint bottle nearly full, seal and label with required data.

---

When a sample is taken by a member of this Association in accordance with the above method, it is requested that he state both upon the label of the sample submitted and upon the analysis blank that "this sample has been taken in accordance with the provisional method of sampling of The American Leather Chemists Association."

The above has been adopted as the provisional method of this Association and each and every member of the Association, when called upon to do official sampling, is requested to sample according to this method.

## PROVISIONAL METHOD FOR LEATHER ANALYSIS

*Sec. 1.—Preparation of Sample.*

The sample of leather for analysis shall be reduced to as fine a state of division as practicable, either by cutting or grinding.

*Sec. 2.—Moisture.*

Dry 10 grams of leather for 16 hours at a temperature between 95°-100° C.

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*Sec. 3.—Fats*

Extract 5 to 10 grams of air-dry leather in a Soxhlet apparatus until free from grease, using petroleum ether boiling below 80° C. Evaporate off the ether and dry to approximately constant weight.

Or, if preferred, extract 30 grams of leather as described above. In the latter case, the extracted leather, when freed of solvent, may be used for the determination of water-soluble material.

*Sec. 4.—Ash*

Incinerate 10 to 15 grams of leather in a tared dish at a dull red heat until carbon is consumed. If it is difficult to burn off all the carbon, treat the ash with hot water, filter through an ashless filter, ignite filter and residue. Add the filtrate, evaporate to dryness and ignite.

*Sec. 5.—Water-Soluble Material*

Digest 30 grams of leather in a percolator over night, then extract with water at 50° C. for three hours. The total volume of solution to be 2 liters. Determine total solids and non-tannins according to the Official Method for extract analysis.

*Sec. 6.—Glucose*

To 500 cc. of the solution obtained by extraction according to Par. 4, add 20 cc. of lead sub-acetate, shake well, let stand for an hour and filter. To 400 cc. of filtrate add dry $Na_2CO_3$ and filter. To the filtrate add 5 cc. concentrated HCl and boil for two hours, allowing the solution to evaporate to about 90 cc. Add dry $Na_2CO_3$ until the solution is about neutral, make up to 100 cc. and filter if necessary.

Take an aliquot part containing not more than .25 gram of sugars, add to 60 cc. of Allihn's Fehling's solution, dilute with water to 145 cc. if necessary, cover with a watch glass, bring to boil and set in a boiling water bath for exactly 30 minutes. Filter through an asbestos mat in Gooch crucible, wash with hot water to free from soluble salts and finally with alcohol, dry 1 hour in water oven, cool and weigh. Multiply the weight of cuprous oxide by .8883 and calculate to glucose according to the following table:

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TABLE FOR THE DETERMINATION OF THE GLUCOSE IN TANNING MATERIALS THROUGH THE COPPER WEIGHED, AFTER HEATING FEHLING'S SOLUTION WITH THE GLUCOSE SOLUTION FOR HALF AN HOUR.

R. Koch and R. Ruhsam. (*J. S. C. I.*, 13, 1227, *et seq.*)

| Cu. Mgrms. | Glucose Mgrms. | Cu. Mgrms. | Glucose Mgrms. | Cu. Mgrms. | Glucose Mgrms. |
|---|---|---|---|---|---|
| 1 | 0.4 | 43 | 18.0 | 85 | 39.2 |
| 2 | 0.8 | 44 | 18.4 | 86 | 39.8 |
| 3 | 1.2 | 45 | 18.9 | 87 | 40.3 |
| 4 | 1.6 | 46 | 19.3 | 88 | 40.8 |
| 5 | 2.0 | 47 | 19.7 | 89 | 41.3 |
| 6 | 2.5 | 48 | 20.2 | 90 | 41.8 |
| 7 | 2.9 | 49 | 20.7 | 91 | 42.3 |
| 8 | 3.3 | 50 | 21.3 | 92 | 42.8 |
| 9 | 3.7 | 51 | 21.8 | 93 | 43.3 |
| 10 | 4.1 | 52 | 22.3 | 94 | 43.9 |
| 11 | 4.5 | 53 | 22.8 | 95 | 44.4 |
| 12 | 4.9 | 54 | 23.3 | 96 | 44.9 |
| 13 | 5.3 | 55 | 23.9 | 97 | 45.4 |
| 14 | 5.7 | 56 | 24.4 | 98 | 45.9 |
| 15 | 6.1 | 57 | 24.9 | 99 | 46.4 |
| 16 | 6.5 | 58 | 25.4 | 100 | 46.9 |
| 17 | 7.0 | 59 | 25.9 | 101 | 47.5 |
| 18 | 7.4 | 60 | 26.4 | 102 | 48.0 |
| 19 | 7.8 | 61 | 26.9 | 103 | 48.5 |
| 20 | 8.2 | 62 | 27.4 | 104 | 49.0 |
| 21 | 8.6 | 63 | 28.0 | 105 | 49.5 |
| 22 | 9.0 | 64 | 28.5 | 106 | 50.0 |
| 23 | 9.4 | 65 | 29.0 | 107 | 50.5 |
| 24 | 9.9 | 66 | 29.5 | 108 | 51.0 |
| 25 | 10.3 | 67 | 30.0 | 109 | 51.6 |
| 26 | 10.7 | 68 | 30.5 | 110 | 52.1 |
| 27 | 11.1 | 69 | 31.0 | 111 | 52.6 |
| 28 | 11.6 | 70 | 31.6 | 112 | 53.1 |
| 29 | 12.0 | 71 | 32.1 | 113 | 53.6 |
| 30 | 12.4 | 72 | 32.6 | 114 | 54.1 |
| 31 | 12.9 | 73 | 33.1 | 115 | 54.6 |
| 32 | 13.3 | 74 | 33.6 | 116 | 55.1 |
| 33 | 13.7 | 75 | 34.1 | 117 | 55.7 |
| 34 | 14.1 | 76 | 34.6 | 118 | 56.2 |
| 35 | 14.6 | 77 | 35.1 | 119 | 56.7 |
| 36 | 15.0 | 78 | 35.7 | 120 | 57.2 |
| 37 | 15.4 | 79 | 36.2 | 121 | 57.7 |
| 38 | 15.9 | 80 | 36.7 | 122 | 58.2 |
| 39 | 16.3 | 81 | 37.2 | 123 | 58.7 |
| 40 | 16.7 | 82 | 37.7 | 124 | 59.2 |
| 41 | 17.2 | 83 | 38.2 | 125 | 59.7 |
| 42 | 17.6 | 84 | 38.7 | 126 | 60.2 |

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| Cu. Mgrms. | Glucose Mgrms. | Cu. Mgrms. | Glucose Mgrms. | Cu. Mgrms. | Glucose Mgrms. |
|---|---|---|---|---|---|
| 127 | 60.7 | 174 | 83.9 | 221 | 107.6 |
| 128 | 61.2 | 175 | 84.4 | 222 | 108.1 |
| 129 | 61.7 | 176 | 84.9 | 223 | 108.7 |
| 130 | 62.2 | 177 | 85.4 | 224 | 109.2 |
| 131 | 62.6 | 178 | 85.9 | 225 | 109.7 |
| 132 | 63.1 | 179 | 86.4 | 226 | 110 2 |
| 133 | 63.6 | 180 | 86.9 | 227 | 110.7 |
| 134 | 64.1 | 181 | 87.4 | 228 | 111.2 |
| 135 | 64.6 | 182 | 87.9 | 229 | 111.8 |
| 136 | 65.1 | 183 | 88.4 | 230 | 112.3 |
| 137 | 65.6 | 184 | 88.9 | 231 | 112.8 |
| 138 | 66.1 | 185 | 89.4 | 232 | 113.3 |
| 139 | 66.6 | 186 | 89.9 | 233 | 113.8 |
| 140 | 67.1 | 187 | 90.4 | 234 | 114.4 |
| 141 | 67.6 | 188 | 90.9 | 235 | 114.9 |
| 142 | 68.1 | 189 | 91.3 | 236 | 115.4 |
| 143 | 68.6 | 190 | 91.8 | 237 | 115.9 |
| 144 | 69.1 | 191 | 92.3 | 238 | 116.4 |
| 145 | 69.6 | 192 | 92.8 | 239 | 117.0 |
| 146 | 70.1 | 193 | 93.3 | 240 | 117.5 |
| 147 | 70.6 | 194 | 93.8 | 241 | 118.0 |
| 148 | 71.1 | 195 | 94.3 | 242 | 118.5 |
| 149 | 71.5 | 196 | 94.8 | 243 | 119.0 |
| 150 | 72.0 | 197 | 95.3 | 244 | 119.5 |
| 151 | 72.5 | 198 | 95.8 | 245 | 120.1 |
| 152 | 73.0 | 199 | 96.3 | 246 | 120.6 |
| 153 | 73.5 | 200 | 96.8 | 247 | 121.1 |
| 154 | 74.0 | 201 | 97.3 | 248 | 121.6 |
| 155 | 74.5 | 202 | 97.8 | 249 | 122.1 |
| 156 | 75.0 | 203 | 98.3 | 250 | 122.7 |
| 157 | 75.5 | 204 | 98.8 | 251 | 123.2 |
| 158 | 76.0 | 205 | 99.3 | 252 | 123.7 |
| 159 | 76.5 | 206 | 99.8 | 253 | 124.2 |
| 160 | 77.0 | 207 | 100.3 | 254 | 124.8 |
| 161 | 77.5 | 208 | 100.8 | 255 | 125.3 |
| 162 | 78.0 | 209 | 101.4 | 256 | 125.8 |
| 163 | 78.5 | 210 | 101.9 | 257 | 126.3 |
| 164 | 79.0 | 211 | 102.4 | 258 | 126.9 |
| 165 | 79.5 | 212 | 102.9 | 259 | 127.5 |
| 166 | 80.0 | 213 | 103.5 | 260 | 128.0 |
| 167 | 80.5 | 214 | 104.0 | 261 | 128.5 |
| 168 | 81.0 | 215 | 104.5 | 262 | 129.0 |
| 169 | 81.4 | 216 | 105.0 | 263 | 129.5 |
| 170 | 81.9 | 217 | 105.5 | 264 | 130.1 |
| 171 | 82.4 | 218 | 106.0 | 265 | 130.6 |
| 172 | 82.9 | 219 | 106.6 | 266 | 131.1 |
| 173 | 83.4 | 220 | 107.1 | 267 | 131.6 |

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| Cu. Mgrms. | Glucose Mgrms. | Cu. Mgrms. | Glucose Mgrms. | Cu. Mgrms. | Glucose Mgrms. |
|---|---|---|---|---|---|
| 268 | 132.2 | 315 | 157.1 | 362 | 183.1 |
| 269 | 132.7 | 316 | 157.6 | 363 | 183.7 |
| 270 | 133.2 | 317 | 158.1 | 364 | 184.2 |
| 271 | 133.7 | 318 | 158.7 | 365 | 184.8 |
| 272 | 134.2 | 319 | 159.2 | 366 | 185.4 |
| 273 | 134.7 | 320 | 159.8 | 367 | 186.0 |
| 274 | 135.3 | 321 | 160.3 | 368 | 186.5 |
| 275 | 135.8 | 322 | 160.9 | 369 | 187.1 |
| 276 | 136.3 | 323 | 161.4 | 370 | 187.7 |
| 277 | 136.8 | 324 | 162.0 | 371 | 188.3 |
| 278 | 137.4 | 325 | 162.5 | 372 | 188.8 |
| 279 | 137.9 | 326 | 163.0 | 373 | 189.4 |
| 280 | 138.4 | 327 | 163.6 | 374 | 190.0 |
| 281 | 139.0 | 328 | 164.1 | 375 | 190.6 |
| 282 | 139.5 | 329 | 164.7 | 376 | 191.1 |
| 283 | 140.0 | 330 | 165.2 | 377 | 191.7 |
| 284 | 140.5 | 331 | 165.8 | 378 | 192.3 |
| 285 | 141.1 | 332 | 166.3 | 379 | 192.8 |
| 286 | 141.6 | 333 | 166.9 | 380 | 193.4 |
| 287 | 142.1 | 334 | 167.4 | 381 | 194.0 |
| 288 | 142.6 | 335 | 167.9 | 382 | 194.6 |
| 289 | 143.2 | 336 | 168.4 | 383 | 195.2 |
| 290 | 143.7 | 337 | 169.0 | 384 | 195.7 |
| 291 | 144.2 | 338 | 169.5 | 385 | 196.3 |
| 292 | 144.7 | 339 | 170.1 | 386 | 196.9 |
| 293 | 145.3 | 340 | 170.6 | 387 | 197.5 |
| 294 | 145.8 | 341 | 171.2 | 388 | 198.0 |
| 295 | 146.3 | 342 | 171.7 | 389 | 198.6 |
| 296 | 146.9 | 343 | 172.2 | 390 | 199.2 |
| 297 | 147.4 | 344 | 172.8 | 391 | 199.8 |
| 298 | 147.9 | 345 | 173.3 | 392 | 200.3 |
| 299 | 148.4 | 346 | 173.9 | 393 | 200.9 |
| 300 | 149.0 | 347 | 174.5 | 394 | 201.5 |
| 301 | 149.5 | 348 | 175.0 | 395 | 202.1 |
| 302 | 150.1 | 349 | 175.6 | 396 | 202.7 |
| 303 | 150.6 | 350 | 176.2 | 397 | 203.3 |
| 304 | 151.1 | 351 | 176.8 | 398 | 203.8 |
| 305 | 151.7 | 352 | 177.3 | 399 | 204.4 |
| 306 | 152.2 | 353 | 177.9 | 400 | 205.0 |
| 307 | 152.8 | 354 | 178.5 | 401 | 205.6 |
| 308 | 153.3 | 355 | 179.1 | 402 | 206.2 |
| 309 | 153.9 | 356 | 179.6 | 403 | 206.8 |
| 310 | 154.4 | 357 | 180.2 | 404 | 207.3 |
| 311 | 155.0 | 358 | 180.8 | 405 | 207.9 |
| 312 | 155.5 | 359 | 181.4 | 406 | 208.5 |
| 313 | 156.0 | 360 | 181.9 | 407 | 209.1 |
| 314 | 156.5 | 361 | 182.5 | 408 | 209.7 |

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| Cu. Mgrms. | Glucose Mgrms. | Cu. Mgrms. | Glucose Mgrms. | Cu. Mgrms. | Glucose Mgrms. |
|---|---|---|---|---|---|
| 409 | 210.3 | 432 | 223.7 | 455 | 239.3 |
| 410 | 210.8 | 433 | 224.4 | 456 | 239.9 |
| 411 | 211.4 | 434 | 225.1 | 457 | 240.6 |
| 412 | 212.0 | 435 | 225.8 | 458 | 241.3 |
| 413 | 212.6 | 436 | 226.4 | 459 | 242.0 |
| 414 | 213.2 | 437 | 227.1 | 460 | 242.6 |
| 415 | 213.8 | 438 | 227.8 | 461 | 243.3 |
| 416 | 214.4 | 439 | 228.5 | 462 | 244.0 |
| 417 | 214.9 | 440 | 229.1 | 463 | 244.7 |
| 418 | 215.5 | 441 | 229.8 | 464 | 245.3 |
| 419 | 216.1 | 442 | 230.5 | 465 | 246.0 |
| 420 | 216.7 | 443 | 231.2 | 466 | 246.7 |
| 421 | 217.3 | 444 | 231.8 | 467 | 247.4 |
| 422 | 217.9 | 445 | 232.5 | 468 | 248.0 |
| 423 | 218.4 | 446 | 233.2 | 469 | 248.7 |
| 424 | 219.0 | 447 | 233.9 | 470 | 249.4 |
| 425 | 219.6 | 448 | 234.5 | 471 | 250.1 |
| 426 | 220.2 | 449 | 235.2 | 472 | 250.8 |
| 427 | 220.8 | 450 | 235.9 | 473 | 251.4 |
| 428 | 221.4 | 451 | 236.6 | 474 | 252.1 |
| 429 | 221.9 | 452 | 237.2 | 475 | 252.8 |
| 430 | 222.5 | 453 | 237.9 | 476 | 253.5 |
| 431 | 223.1 | 454 | 238.6 | | |

## *Sec. 7.—Nitrogen*

Gunning modification of the Kjeldahl Method, A. O. A. C. Bulletin, No. 107 (1907).

### *Reagents.*

*Standard Acid Solutions.*—Hydrochloric or sulphuric acid, the absolute strength of which has been accurately determined. For ordinary work half-normal acid is recommended. For work in determining very small amounts of nitrogen, tenth-normal is recommended. In titrating mineral acids against ammonium hydroxide solution use cochineal as indicator.

*Standard Alkali Solution.*—The strength of this solution relative to the acid must be accurately determined; tenth-normal solution is recommended.

*Sulphuric Acid.*—The sulphuric acid used should have a specific gravity of 1.84 and be free from nitrates and also from ammonium sulphate.

*Sodium Hydroxide Solution.*—A saturated solution of sodium hydroxide solution free from nitrates.

*Potassium Sulphate.*—This reagent should be pulverized before using.

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*Indicator.*—A solution of cochineal is prepared by digesting and frequently agitating 3 grams of pulverized cochineal in a mixture of 50 cc. of strong alcohol and 200 cc. of distilled water for a day or two at ordinary temperature; the filtered solution is employed as indicator.

*Determination.*

Place .7 gram leather in a digestion flask. Add 10 grams powdered potassium sulphate and from 15 to 25 cc. (ordinarily about 20 cc.) of concentrated sulphuric acid. Place the flask in an inclined position and heat below the boiling point of the acid for from 5 to 15 minutes, or until frothing has ceased (a small piece of paraffine may be added to prevent extreme foaming).

Then raise the heat and boil briskly until the liquid has become quite clear and nearly colorless (the digestion should take from 4 to 5 hours).

After cooling, dilute with about 200 cc. of water. Next add 50 cc. soda solution, or sufficient to make the reaction strongly alkaline, pouring it down the side of the flask so that it does not mix at once with the acid solution. Connect the flask with the condenser, mix the contents by shaking, and distil until all ammonia has passed over into the standard acid. The first 150 cc. will generally contain all the ammonia. The operation usually requires from 40 minutes to 1 hour and a half. The distillate is then titrated with standard alkali.

Previous to use, the reagents should be tested by a blank experiment with sugar, which will partially reduce any nitrates present that otherwise might escape notice.

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## THE GELATINE-SALT TEST FOR TANNIN

BUCKFASTLEIGH, DEVON, 1st Oct., 1907.

*The Editor, Journal of Am. Leather Chemists' Ass'n.*

DEAR SIR:

I have had your May's issue for some time before me with the intention of examining Mr. Reed's paper in which he criticizes some of my work bearing upon the assay of tannins. I am now at liberty to reply to him if I have your permission to do so.

Regarding the first part of Mr. Reed's paper, there is very little that I can say, for his results with my test are so completely at variance with those found by me as to make a reconciliation

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of the two to appear impossible. Although apparently done on my lines, there must be something very different somewhere to produce results so antagonistic.

This difference may lie (1) in the state of the gelatine; (2) in the strength of the acid; (3) in person. The last possible cause for the difference I think may be discarded as there are so many observations on either side recorded, nearly all of these being different. I don't think I gave the strength of the acid in my paper, but I used the ordinary concentrated acid diluted one in four. With my gelatine the strength of acid used was such that had the strength been increased by ten olr fifteen per cent. there would have been a considerable floccuent precipitate of gelatine without any tan at all. I think I stated in the paper that the acidity was such that the gelatine was just on the point of precipitating. Now it stands to reason that if even such a slight amount of a colloidal body like tan be added to another colloidal body like gelatine just on the point of breaking up into its insoluble form, the balance of solubility will be upset, and the tan will form a precipitate. I am therefore quite convinced that the conditions as used by Mr. Reed were not those used by me, for he gets no precipitate even with the stronger tan solutions. Did Mr. Reed's mixture of 5 cc. of water, 10 cc. of gelatine, and 1 cc. of dilute hydrochloric acid precipitate when two drops, or yet five drops more of the dilute acid were added? If it did not, and I expect it did not, judging from his results, then there is no comparison at all between his results and mine. They are on entirely different footings. If it did I shall be glad to go into the matter further. I can well understand gelatine varying as regards the amount of acid necessary to precipitate it. Even the same gelatine varies considerably with time when in solution. In Mr. Reed's reference to Sutton I take it that the latter wishes to indicate a strong saline solution apart from its nature. This is provided in the test by the salt. I still affirm that a precipitate is much more satisfactory and reliable for observation than opalescence. I think this disposes of Mr. Reed's paper so far as his remarks referring to my test are concerned.

Regarding Mr. Reed's remarks upon the higher percentage of non-tan as given by ordinary hide powder over chromed, this surely requires no explaining, for chromed powder is well

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known to be less soluble than ordinary powder. A correction always has to be applied for the varying solubility of the latter, affecting the result from one to two per cent. for ordinary good powders. Still, I do not deny that the relative insolubility of chromed powders is not in favor of its use, when this fact is viewed alone.

Mr. Reed goes on the question of equilibrium; but his remarks are vitiated by the fact that his test for tan in the detannized filtrate is deceptive. The residue of tan after detannizing is not only small in amount, but weak in character, and, as I pointed out, is not to be compared with a fresh solution of the same strength. I am prepared to separate tan in any liquors so detannized in amount of the order of magnitude of what I have already indicated as being present in them. I do not think Mr. Reed quite grasps the equilibrium problem. At any rate I never experienced an action of absorption followed by a subsequent reverse action of effusion in one and the same system, and I do not think I stated that such a reversal took place in a non-tan determination. When brought into a weaker liquor, the reverse action is experienced whether the hide be much or little tanned. I also fail to see that an excess of hide makes an equilibrium impossible. Hide has a great affinity for tan, but that affinity is limited, and is especially weakened in the dilute solution used for detannizing. Also, how can there be, as Mr. Reed says there is, fresh hide continually presented to the solution in the shake method? If there were, I should not have anything to say against the shake process. The hide powder is presented all at once.

I quite admit that the old filter-bell method is defective, especially as regards the partial solution of the powder, but I considered, and still consider, the new method to be equally so; and as I couldn't see any improvement to be gotten by changing, I opposed the change as much as was in my power, which wasn't much. It did not appear to me to be a change in the right direction at all. Considering that hide powder is notoriously varying in character, it is obviously desirable to diminish the effect of the variation on the analysis. Also, the amount of hide powder used in our old method is about ten times the amount required to produce a lightly tanned powder, and that in the new method about double as much. Any effort at improving

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the method of analysis must aim at reducing the effect of the variation of the powder, and this is not accomplished by increasing the amount of powder used. It is indeed questionable whether the degree of uniformity obtained by chroming the powder is such as to make good the increased liability of error through using double the amount of it. A method of analysis in which only a slight amount of the powder is used must be aimed at. This can be accomplished by separating nearly all the tan with a little powder, and estimating the residue by applying the law of equilibrium, the constants of which may be obtained by experiment once and for all. These constants do not vary very much, and the ultimate error is very small as it is the product of two small quantities—the amount of tan left in the liquor, and the small variation in the equilibrium constant—especially small in very weak liquors.

Apologizing for this long letter, I am, dear sir,

Yours truly,

ROWLAND A. EARP.

## INTERNATIONAL ASSOCIATION OF LEATHER TRADE CHEMISTS

*Meeting of the German Section, Sept. 22, 1907, at Frankfort-a-M.*

(*Collegium, 1907, 279, 280, 365, 369.*)

The meeting was opened by Prof. Dr. Becker who welcomed the members present, after which the reports of the Secretary and Treasurer were read, followed by the election of officers, which resulted in the reelection of the officers of the previous year. Mr. K. Schorlemmer then read a paper on the new international method of tanning analyses, in which he stated that he considered the new official method of the I. A. L. T. C. to be a decided advancement. After the reading of the paper a lively discussion ensued in which Mr. Mueller declared in the name of the Association of Extract Manufacturers to be unable to accept the new method at present. This could be done only when the difference between the results of the filter-method and the shake-method could be accurately determined. The speaker further stated that the old method gave good and concordant results of late which probably were due, at least in the German Section, to the fact that all details, such as form and size of the dishes,

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drying ovens, etc., were alike. These detailed rules were missed in the new method, which is a decided disadvantage. According to past experiences, the differences in comparative analyses with both methods are not concordant, not only with different tanning materials but also with the same tanning material, so that until now no definite relationship between the two methods could be determined. The extract industry therefore could not give their consumers a guarantee if the shake method be used as a basis, and therefore for the present must insist that in those cases where contracts are closed with members of the Association of Extract Manufacturers that the filter-method be used. The president then stated that as well as the irregularities which first appeared with the filter-method were overcome, the same will also be overcome with the shake-method with the help and good-will of the extract manufacturers. Dr. Paessler stated that he does not consider the shake-method to be superior to the filter-method and gave the results of analyses made at the German Experiment Station for Leather Industry which showed that with different tanning materials and different samples of the same tanning material the differences between the results of the filter-method and shake-method vary greatly, so that no definite relationship exists, which naturally makes the change to the shake-method more difficult. In his opinion there was no real reason to replace the filter-method by the shake-method. Mr. Renner agreed with Mr. Mueller in his remarks. Mr. Hugendubel stated that he fears new difficulties will arise. Prof. Dr. Philip pointed out that in the regulations it is not especially stated whether only a white hide powder can be used and the same chromed before the analysis, or whether the chromed hide powder, made at the Freiburg Experiment Station, could also be used. In his opinion the chroming of the hide powder is too cumbersome, and the use of the ready chromed hide powder gives closely agreeing results. Dr. Paessler corroborated this and states that by using the chromed hide powder he obtained the same results as by using the hide powder chromed before the analysis. After debating further on this subject a committee was appointed, consisting of Dr. Klenk, Dr. Moll, Dr. Paessler, Mr. Roser and Dr. Sichling, which was instructed to thoroughly test the shake-method and to make such recommendations as would tend to give greater concordance of results.

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The committe is to report next year at the spring meeting. Dr. Paessler then presented a paper on the tensile strength of chrome leathers of different tannage and different lengths of storing, giving an account of a series of experiments which he conducted and which showed that with the different tannages and different lengths of storing, the tensile strength is not impaired. Following this paper, Mr. P. Kauschke read a paper on the neutralization of chrome leather which was succeeded by a paper by Prof. Dr. Becker on the stability of neats-foot oil in the cold. Dr. Paessler then read a paper entitled "Proposals for the Uniform Determination of the Solubility of Tanning Extracts." In the discussion which followed, Mr. Schorlemmer stated that in such tests not only should the amount of the substances which have gone into solution be considered, but also the constitution of the same, as in practice it makes a great difference whether these substances are of a resinous or flocculent nature. Dr. Bedford then gave an account of his method for determining the moisture in different substances, which consists in working at ordinary temperature in a vacuum at an air pressure of 1/1000 mm. This method requires liquid air or solid carbonic acid, and a determination can be carried out in about half an bour. The meeting then adjourned.

*Meeting of the British Section.*

A meeting of the British Section of the I. A. L. T. C. was held in the club room at the Shoe and Leather Fair, Islington, on Thursday, November 7th. Professor Procter, president of the section, presided.

At the commencement of the proceedings Dr. Parker gave a condensed report of the Conference of the American Leather Chemists held in Chicago, which he attended as a delegate of the I. A. L. T. C. He described several methods and apparatus used by the American colleagues. The statement that the American Leather Chemists' Association had appointed a standing committee to work with a corresponding committee to be appointed by the Executive Committee of the I. A. L. T. C. for the purpose of unifying and standardizing the methods between the two associations was received with great satisfaction. Messrs. Procter, Bennett, and others expressed their great pleasure of the possibility of establishing standard methods of analysis in connection with the leather trade for the whole world.

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### Dr. Parker on the New Method of Analysis

Dr. Parker then explained for the benefit of the tanners and extract manufacturers present the reasons for adopting the new method of analysis, and also explained the reasons for the differences which were obtained by the two methods. He pointed out that this was not a sudden change, but a matter which had been under deliberation for seven years, and that it was only after mature consideration, and as a result of long, painstaking work by a commission, that the association had been compelled to break away from the filter-bell method, which had been proved to be inaccurate and misleading, and depended on two factors—both of which were at all times variable—*viz.*, the quality of the hide powder, which could never be the same, and the personal element of each chemist. He claimed that the new method gave results more in accordance with the results obtained in the tannery. This had been abundantly proved not only in America, where they had used the method for years, but it had also been proved by several of the tanners of this country. He explained that although a change in the method of analysis would for the next few months be confusing to the trade, yet he was perfectly sure that when the tanners and extract manufacturers got accustomed to the method, they would soon see its immense advantages, and that more concordant results would be obtained by different chemists analyzing the same sample than was ever possible under the old method.

Mr. Bennett, in bearing out Dr. Parker's remarks, said that the extract manufacturers would find that they would gain more information by using the new method in their factories than they obtained by the filter-bell method. He pointed out that two chestnut or other extracts both analyzing by the filter-bell method 30 per cent. need not necessarily give the same figures by the new shake-method. One might give 28 per cent. and the other might vary 1 per cent. up or down. It would depend largely on the method of manufacture, the temperature of extraction, and concentration. But that in the manufacture of extracts some of the tannins might be altered in some way, that although they were absorbed by the filter-bell method, not being true tans they would not be absorbed by the new method, and argued that they would not be absorbed in the tanyard either.

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### Professor Procter Supports the Change

Professor Procter pointed out that no definite ratio could be fixed between the two methods, excepting on certain definite extracts. It would be necessary for extract manufacturers to each work out the difference by their own special brands of extract, that although a general difference did exist, one could not lay down any specific figure. He said that if any figure could be given, there would be no need to alter the method. As the inventor of the filter-bell, he claimed that it ought to be a strong argument in favor of the new method if he, as the inventor of the old method, was forced to acknowledge that although it had served its purpose, it was now proved to be inaccurate and misleading.

A long discussion took place, in which the extract manufacturers present joined.

In summarizing the discussion, Dr. Parker pointed out that the new method of analysis was now practically the same as the official method of the American Leather Chemists' Association, and that although it differed in one or two details, it gave practically identical results. He claimed that this was an immense advantage to Europe, as America had in the past few years become large purchasers of European tanning materials, and the adoption of a uniform method of analysis would greatly facilitate trade, which ought to be beneficial to the whole of Europe.

An adjournment took place at 12.30 to enable a deputation of the chemists to attend a meeting of all the federations of British tanners, which was held at the Midland Hotel.

Professor Procter, Dr. Parker, and Dr. Turnbull again explained the reasons of the change in the method of analysis to the tanners, and said that no definite figure could be given to cover all extracts as indicating the difference between the two methods. They stated that analyses could be done by the two methods side by side until the end of the present year, but that after that it would be impossible to carry out any further analyses by the filter-bell method as the supply of satisfactory hide powder for this purpose has now ceased.

### An Important Resolution

Various questions were asked by the tanners present and replied to. The chemists were cordially thanked for attend-

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ing and for explaining the various matters, and were assured of the hearty support of the tanning trade of Great Britain and Ireland.

In the afternoon the meeting of the British section was resumed, and after a further general discussion, in which Messrs. Walker, Gates, Hough, Campbell, Rink, O'Brien, Wood, and the Chairman took part the following resolution was passed unanimously:

"The British Section note with regret the resolution of the Association of German Extract Manufacturers to guarantee delivery only on the analysis of their own nominated chemists done by the filter-method with chromed hide powder. The British Section points out to its members that the prescribed method has never had the official sanction of the International Association of Leather Trades' Chemists; and has been specifically condemned by the International Commission and the Executive Committee of the Association as giving too high results; and the analyses of the Association of German Extract Manufacturers must therefore be received with the usual reserve accorded to sellers' analyses made by an unauthorized method."

Several members then expressed the hope that every member and associate of the British Section would abide loyally by every detail of the rules of the association, and that they would assist the trade by doing everything to facilitate the change in the method of analysis which had recently been made, and endeavor to familiarize the trade with the advantages of the new method.

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## THE QUESTION OF TANNIN ANALYSIS

(From *The Leather Trades Review.*)

DEAR SIR: In your issue of October 2nd, page 699, you published an interesting leader on "The Problem of Tannin Analysis,"[1] and there has also since that time been some correspondence in your columns on the same subject. Perhaps you will allow me, therefore, a few remarks which may tend to clear up the difficulty. I may remind you that the new method of analysis, which is an improved form of the American shake-method, has been adopted officially by the International Association of Leather Trades' Chemists, after very prolonged consid-

[1] THIS JOURNAL, 1907, p. 448.

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eration and thorough testing and examination by the best body of experts which the association could get together, including not only its own members, but other chemists from Europe and America. The decision of this Commission was practically unanimous in favor of the necessity of a change, and of the new method which was then introduced. The credit for this method cannot be allotted to any one individual or any one nation. The employment of hide powder for the purpose dates from Hammer and other chemists well back in the last century. Its use for a gravimetric method was first shown to be practicable by the Vienna Research Institute under Director Eitner, and this institute also introduced later the use of chromed hide powder, while the Americans contributed the employment of a mechanical shaker in place of mere stirring, and have done much to improve details since they have adopted the method as official. The International Commission in their deliberations had the assistance both of Director Eitner and of leading American chemists, and had the whole of this great mass of material at their disposal, and, in addition, carried out very laborious experiments with a view to the thorough testing of the method. It is clear that the change has been the result of no hasty decision, nor does it adopt a new and untried method. It is, therefore, more than a little calculated to arouse the interest of tanners when we find that the Association of German Extract Manufacturers is endeavoring by all means in its power to oppose the use of a new method which has been tested and approved by a very large majority of the leather trades' chemists of the world as giving more accurate and therefore lower results in tannin, since it has long been known that the hide powder used in the filter removes from a liquor certain substances which are not tannins and cannot produce leather, and that this is done to a much diminished degree by the improved shake method. It is even somewhat natural that the tanner should suppose that the true objection of the extract manufacturers is not that the results are not accurate or concordant, but that they are lower and calculated to give the tanner a better judgment as to the value of their products.

I am frequently asked at present what is the difference for any class of extracts between the old and the new method, and it has often been urged that the new method cannot be adopted

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unless this information can be definitely given. My reply is that if this were possible there would be no need for any change, but that the very fact that the new method does not estimate the non-tanning substances which were included by the filter-method makes any such statement impossible, since these non-tanning substances vary from extract to extract and from one brand to another. It may, indeed, be pointed out that, other things being equal, more of these matters will be found in a badly manufactured than in a well manufactured extract, since they are largely the result of the destruction of tannin during the manufacturing process, and that consequently it is to the interest of the inferior manufacturers to adhere to the old method. Of course, I do not forget that among the non-tannins are included sugars, which are useful to the tanner as a source of acid in his liquors, but these are to no large extent estimated either by the older or the newer method, and it is mainly bodies such as gallic acid which come into consideration. In this connection it is perhaps fair to mention that I have had no complaints or objections from the English extract manufacturers, excepting so far as their fears have been raised as to the want of concordance of results, and as a general rule in the better brands of extract the differences introduced are extremely small.

As regards the question of concordance of the analyses of different chemists, it may be remarked that complaints have been made about inaccuracies by the new method which would have been taken as a matter of course with the old one. In 1903, (*Collegium*, p. 143) Dr. Paessler and other chemists agreed that differences up to 1½ per cent. on ordinary liquid extracts and 3 per cent. on solid were permissible and to be expected. With the newer method complaints are being made of differences even of 1 per cent. only, with substances of high percentage such as quebracho extract. While I believe that, as a general rule, accuracies approaching 1 per cent. and often much closer can be obtained, it is unreasonable to expect in the difficult region of tannin analysis an accuracy which is attained in few other branches of analytical chemistry. The attention of tanners may also be directed to the point that in many cases the differences found are not due to variations in the determination of the "non-tanning matter," which is the only point effected by the shake-method, but rather on questions of filtration and the

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determination of insolubles, which equally affect the result in tannin, but which have only been altered by the Commission in the sense of giving a stricter definition of what was to be regarded as a "clear solution."

Of course, it is inevitable that on the introduction of a new method a certain number of careless chemists will make errors by not following the instructions with sufficient closeness. That this is actually the case I have unfortunately had evidence in correspondence, and I may point out that small deviations from the methods described for washing, weighing and calculation may in some cases produce material errors.

Turning from your leader to a letter on tannin analysis on page 749 of your paper, I would ask the writer who objects to the new shake-method, but is not a chemist, whether he can suggest any method which is free from the objections which he raises? It is impossible to estimate tannin in time to be of value to the trade by a tannin process which would extend over weeks, and the chemist is obliged to adopt other methods, and these methods have been shown to give accurate and constant information which is of great value to the tanner who uses them intelligently. There is, however, much in "Enquirer's" letter in which every capable leather trade chemist would agree. The question of the actual amount of tanning matter in an extract or material is not by any means the only one which determines its value, though it furnishes reliable information as to which of two samples of the same material will produce the largest amount of leather. The reasonable tanner knows very well that he cannot substitute sumach for valonia or *vice versa*.

There are some tans which, while capable of converting a large amount of hide powder into leather, are not capable of giving great weight or solidity even if used in large quantities, and there are two questions, the answers to which are very different but which are often confused in the tanner's mind. Firstly, how much leather will a pound of a given extract produce? and, secondly, how much leather can be produced by a given extract from a pound of hide? The first of these questions is answered with fair accuracy by an analysis of the extract; the second, if it can be answered at all out of the tannery, by a quite different sort of experiment.

As regards the point which "Enquirer" raises as to the differ-

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ence between hide powder and hide in its absorption of tannin, I think that this has been much exaggerated. The tanner himself uses dry hide, which he suitably soaks before tanning, and so does the chemist, and this is especially the case by the shake process as compared to the filter-method. The principal difference between hide powder and hide is that the former, being finely divided, can be much more completely exposed to the action of the liquor than the latter, and consequently a much quicker tannage can take place. A much sounder objection, and one which every chemist must admit, is that no rapid process in the laboratory can obtain exactly the same results as the slow and somewhat haphazard methods of the tanner. "Enquirer" concludes by a remark which is somewhat characteristic of the non-chemist, saying in one breath that it is surely time the question of tannin analysis was settled once and for all, while he admits that chemists have been working at it for many years. Possibly he will come to our assistance, and settle the question.

Yours faithfully,

HENRY R. PROCTER.

LEATHER INDUSTRIES DEPARTMENT,
LEEDS UNIVERSITY, LEEDS.

## REVIEWS

**On the Neutralization of Chrome Leather.** P. KAUSCHKE. *Collegium*, 1907, 278, 279, 354, 357.—It is evident that every chrome leather, tanned either by the one-bath or two-bath process, must be neutralized by the use of chemicals as the washing out of the acid with water alone is not sufficient. Consequently, substances must be used of weak alkaline reaction such as sodium bicarbonate, borax and sodium phosphate. Ammonium bicarbonate can not be used as this salt, though its dissociation acts similar to ammonia. Borax is generally used while sodium bicarbonate and sodium phosphate have so far not been sufficiently valued. Borax and sodium phosphate act in an analogous way, for in both an acid, boric acid or phosphoric acid, is liberated by the mineral acid in the leather, which is seen from the following equations:

$$Na_2B_4O_7 + 2HCl + 5H_2O = 2NaCl + 4H_3BO_3$$
$$Na_2HPO_4 + 2HCl = 2NaCl + H_3PO_4.$$

If for the neutralization of a chrome leather 2 kg. of borax per 100 kg. are necessary, then 1.30 kg. of free boric acid are formed. In case sodium phosphate is used instead of borax, for the same chrome leather, 1.87 kg. are only necessary, which would form only 0.51 kg. of free phosphoric acid. This shows it is more advantageous to use sodium phosphate than borax.

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In order to determine what further action these acids exert, a series of experiments were carried out by the author. When using sodium bicarbonate, the liberated carbonic acid escapes and so can not have any action on the tannage. The experiments showed that with borax and sodium phosphate a real neutralization can not be achieved. When using sodium phosphate this can be seen at once by the acid reaction of the solution tested with litmus paper. The boric acid formed when using borax is more dangerous, as this cannot be recognized as free acid. It is advisable that chrome leather which has been neutralized with borax should be well washed before further procedure. Furthermore, the results showed that chrome leather at a higher temperature requires more neutralizing material than can be considered profitable, so that in all cases it is advisable that the neutralization is carried out at ordinary or slightly warm temperature. The author states that in case he should recommend a method which would give better results, it would be that the leather should first be treated with sodium phosphate, the liquor then allowed to drain off and then treated with a weak solution of sodium bicarbonate. The temperature of the solutions should be between 20° and 30°. The amounts of sodium phosphate and sodium bicarbonate must be determined in every chrome leather tannery by a special test, also the length of the action determined. The author states that he neutralized in this way three chrome leathers, one from the one-bath process and two from the two-bath process and obtained with all a perfect neutralization by using the following amounts: 100 kg. of leather are treated for half an hour in the wheel with a solution of 2250 grams of sodium phosphate in 100 liters of water at a temperature of about 25°. After this the liquor is run off and the leather wheeled for a quarter of an hour with a solution of 50 grams of sodium bicarbonate at the same temperature. The benefits to be derived from this procedure are that the acid removed from the basic chrome salts by excessive neutralization is replaced by phosphoric acid and the chromium phosphate thus formed is insoluble in water as in the weak acids which are used in the dyeing. Further that the free phosphoric acid can readily be removed by a very small amount of sodium bicarbonate without having any action on the leather.

**A New Method of Tanning.** *La Conceria.*—This method consists of the treatment of hides and skins with a basic solution of chrome alum, of chloride of chrome and a tanning extract. The inventor claims that this system of tannage can be used for glossy leather as well as for colored leather ("fleur"). Five kilos of chrome alum are dissolved in 15 liters of water, and this is mixed with a solution of calcined soda dissolved in 5 liters of water. The mixture is slowly poured into a pit fitted with paddles, which has first been partly filled with water heated to a temperature of 27 to 30° C. The skins are then placed in it, after they have been suitably prepared, and they are kept on the move for four hours. The skins are afterwards treated in a second bath containing a solution of chrome hydrate dissolved in 5 liters of hydrochloric acid and mixed with a solution of soda in order to separate the basic chromic oxide. The skins are subsequently folded and milled in a fuller. Then they are washed and put into a series of tannic baths, composed of sumac, gambier and quebracho in variable proportions. This

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operation can be carried out in revolving drums and takes about six days, after which the finishing is proceeded with.

**Dongola Calf.** *Allg. Gerb. Ztg.*—The skins are sorted, trimmed and soaked in the usual way. The limes are made as follows: 85 pounds of lime are slaked and added to 15 pounds arsenic sulphide and mixed in a barrel containing 50–60 gallons of water. This amount is to be used for 200 calfskins weighing from 8–12 pounds a piece or for 250 calfskins weighing from 6–8 pounds a piece. For starting the limes, 4 per cent. of this mixture is used and strengthened every day for four to six days. As soon as the hair slips easily, the skins are dehaired either by hand or machine. They are then washed with lukewarm water, fleshed, grain smoothed and bated. Then washed out of bate and drenched for three-quarters of an hour in bran and wash. The skins are now ready for tanning. The liquor is made up as follows: For every 25 gallons of water add 2 pounds gambier, ½ pound alum and 6 ounces salt previously dissolved in water. In the tanning liquor which is daily strengthened, morning and noon, the skins are wheeled. The daily strengthening material equals the amount of the fresh liquor. After remaining in the tan liquor eight days, the skins are horsed and allowed to drain over night. In the morning, they are stuffed with a mixture of 18 quarts cod oil and 18 quarts bone fat (tallow) for 250 skins. After one hour they are removed from the drum and dried in a warm room. The dry skins are then folded or piled and allowed to sammy for 5–6 days. They are then moistened on the flesh with a weak tanning solution and carefully smoothed and softened in lukewarm water. Retanned in a 2–3° Bé. sumac, quebracho, oak or mimosa liquor for three to four hours in the drum. Dried and then staked and refatliquored with 180 quarts water, 23 quarts stuffing mixture for 5 dozens skins. If it is desired to have a yellow back the skins can be colored with auramine O or turmeric before the second stuffing and then dried and blacked on the grain; dry, stake and finish.

**The Cold Test of Neatsfoot Oil.** H. BECKER. *Collegium*, 1907, 283, 393.—The author gives an account of the different methods for determining the cold test of neatsfoot oil and shows that the same vary greatly. In order to get an official method for this determination the author suggests the following method for adoption: An 18 mm. wide test-tube is filled with the neatsfoot oil to be tested, from which the water has been removed with calcium chloride and subsequent filtration through a dry filter-paper. An accurate thermometer is then inserted and held by placing the same through a cork so that the bulb comes in the middle of the oil. The sample is then placed, together with a sample of the oil from which the water has not been removed, in a cold mixture which has the minimum temperature guaranteed. If after an hour the oil remains liquid and clear it comes up to guarantee. An oil containing much water or one with a sediment on the bottom of the sample would be sufficient cause for a claim, and from the comparison between the oil before and after removal of the water a decision regarding this can readily be made. The author has found that oils which should have had a cold test of —10° C. became more and more turbid from —1° which was due to a small amount of water that had gotten into the sample either

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by the bottles not being absolutely dry or the barrels containing small amounts of water. These oils after treatment with calcium chloride and filtered through a dry filter-paper then came up to guarantee.

**On the Past Methods for the Determination of Tannin without the Use of Hide Powder.** E. STIASNY. *Der Gerber*, 1907, 787, 789, 790, 792, 794, 795, 796, 169, 199, 213, 241, 269, 283, 295.—The author gives an account of the numerous methods proposed in the past for the determination of tannin, and classifies the same in I, precipitation methods; II, oxidation methods; III, colorimetric methods; IV, absorption methods (without hide powder); and V, other methods. The precipitation methods with gelatine or albumen are not correct as it has been shown that the composition of the precipitates of two colloids is very irregular and, according to Mulden, the proportion of the precipitation, when the tannin solution is run into an excess of gelatine solution, is 100 parts of gelatine: 85 parts of tannin and when carried out in the reversed way it is 100 parts of gelatine: 134–136 parts of tannin. The variations in the proportion of the precipitates can furthermore be seen by the non-agreeing results of different investigators. Groeger states that 42.74 parts of glutin combine with 57.26 parts of tannin, Bottinger's gelatine-tannate contains 34 per cent. of tannin, according to Jean's assertions 53 per cent. of tannin, and according to Davy's recalculation factor 40 per cent. of tannin. The non-tannins also have an influence on the tanno-gelatine precipitate, and this can be observed by adding to a tannin solution which has been so strongly diluted that with gelatine-salt solution a turbidity is only produced, a solution of oak wood non-tannins, and on addition of the gelatine solution, a flocculent precipitate will be obtained. The non-tannin solution which alone does not give a precipitate with gelatine and remains clear, is precipitated in presence of even small amounts of tannin. All these older methods are therefore incorrect and useless, and this also applies to a new method proposed by Parker and Payne in 1904. According to Parker and Payne the tannins are precipitated with a more or less peptonized gelatine, called "collin." The errors which result in this method are the same as described in the others, only with the addition of several more. According to the method given, 200 cc. of the tannin solution should be precipitated with 100 cc. of collin solution and 100 cc. of N/5 acetic acid, filtered and to 200 cc. of the filtrate 200 cc. of N/5 lime solution added, shaken, allowed to stand closed for one hour, and 100 cc. of the filtrate titrated back, making a deduction for the originally added acetic acid. This deduction is made with the supposition that the acetic acid went through all the operations and into the filtrate without being decreased except by dilution. This supposition is undoubtedly wrong, as the tanno-collin precipitate will surely absorb acetic acid. The author then speaks of the methods by precipitation with alkaloids and quotes the methods of Davy, Wagner, Crouzel, Trotman and Hackford. In regard to these methods the author states that it must be considered a great advantage that the precipitant is a definite chemical compound and the precipitate of definite composition, but it also must be remembered that the alkaloid compounds were only isolated and analyzed from gallo-tannic acid, and

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nothing is known of the alkaloid compounds of other tannins, which fails to give the methods a sound foundation. The author then goes over to the precipitation with inorganic compounds and states that in the oldest methods, copper and iron salts were used as precipitants. The advantage in these methods can also be considered the definite composition of the precipitants. It is questionable though whether these precipitation products really possess the advantage spoken of, and in conjunction with this question the author quotes the works of Hantzsch and Desch, Desmouliere and Wittstein. The methods described are those of Handtke, Rouss, Fleck, H. Sackur, E. Wolff, Gawalowsky, W. F. Dreaper, Gerland, Risler-Bennat, Manea, Villon, Barbieri, Carpene, Kramszky, H. Krug and S. C. Dodge. In speaking of other methods, the author gives those of Specht and Lorenz, for dyeing purposes, who precipitate the tannin with safranin and tartar emetic, which cannot be recommended, and Noelting and Feder who use basic dyes. The author then speaks of the various suggestions which have been made, based on the formation of insoluble condensation products of some tannins with formaldehyde and hydrochloric acid. According to work of the author the formaldehyde precipitation is not suitable as a general method as only the protocatechu tannins are transformed into insoluble condensation products. But also for the protocatechu tannins this method is not suitable as on heating the water extraction of the tanning material with hydrochloric acid and formaldehyde the non-tannins are also precipitated. Nevertheless, P. Etschegorry and Jean and Frabot have recommended this method. The author then speaks of the oxidation methods and refers to the one by Lowenthal. Of more recent data are two suggestions which are similar to the old method of Mittentzwey. One of these is Thomson's method which consists in determining tannin by the absorption of oxygen. Another similar method is the one by Vaubel and Scheuer which has the same fault as the other methods as it is based on the absorption of gallo-tannic acid. The author states that the amount of oxygen absorbed by 1 gram of tannin as given by Mittentzwey, Terreil and Vaubel vary greatly, as according to Mittentzwey 1 gram of tannin absorbs 175 cc. of oxygen at 20° equal to 163 cc. at 0°, according to Terreil and Thomson 200 cc. at 0° and 760 mm. and according to Vaubel 229 cc. at 0° and 769 mm. It is evident from work which has been done that the oxidations are too complicated and uncontrollable in order to base an analytical method on the same. Other methods for the determination of tannin which are based on the absorption of iodine by tannins are those of Boudet, Jean, Musset and Commaille. The author states that the iodine absorption for the determination of tannin cannot be used in this way as the amount of iodine used, as shown by Boettinger, is dependent on the concentration of the iodine solution. The author then speaks of an observation which he made when heating tannin solutions with an iodide-iodate mixture and states that any tannin solution, after adding iodide-iodate mixture and thiosulphate in excess and boiled a short time, will darken and the cold solution will no longer give a precipitate with gelatine-salt. The reaction was tried with tannin, oak wood, chestnut, pine, mimosa, quebracho, mangrove, valonia and myrabolams, with solutions of the usual analysis strength and adding to 50 cc. of the solutions 10 cc. of a 10 per cent. potassium iodide

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solution and a freshly prepared solution of .5 gram of potassium iodate, after which 30 cc. of about a N/10 thiosulphate solution was at once run in and the contents of the flask boiled a few minutes. After cooling a negative gelatine reaction was in all cases obtained. A tanning test also showed that a solution of chestnut treated in the same way lost its tanning power, as a piece of skin placed in this solution was well colored through but not tanned, a parallel test with the untreated chestnut solution giving a tanned piece of skin in the same length of time. Tannin solutions boiled with thiosulphate alone do not give the stated phenomenon so that the iodide-iodate mixture must cause the same. The author explains this phenomenon in such a way that through the iodide-iodate mixture, with liberation of iodine, compounds are formed of a salt-like nature. These salt-like compounds do not give a precipitate with gelatine and have no tanning action and as shown by an experiment have increased dialyzing property. The author then speaks of colorimetric methods and quotes those of Wilderstein, Schluteg and Neumann, Jean and Hinsdale which consist in measuring the tannin by the dark colors produced by iron salts. These methods do not come into consideration for the leather industry but for the manufacture of inks. In speaking of adsorption methods the author states that such substances as glue-free raw silk, prepared violin strings, albumen, formalin-gelatine, freshly precipitated iron hydroxide and aluminum hydroxide, sprouted alumina and casein were used.

**Insoluble Gelatine.** R. A. EARP. *Collegium*, 1907, 281, 379.—The author compares the action of the colloids with the process of tanning and gives an account of the action of tanno-gelatine and of experiments made on the solubility of gelatine, stating that it is already fully recognized that prolonged heating causes gelatine to lose its power of gelatinizing which means it changes gelatine in a sense opposite to that of solidification or gelatinization, and which may be called the negative sense, the direction toward solidification being called the positive sense. Gelatine, under aseptic conditions however, does appear to undergo transformation towards the permanent insoluble condition, with no other external agency but that of time alone. The results indicate that the action of time on gelatine seems to render the same more insoluble. The author states that new gelatine precipitates relatively much more tannin than old gelatine does and that the reaction with tannin indicates that gelatine with time becomes changed towards the condition of dried hide-substance.

**Barbatimao Bark.** *Der Ledermark*, 1709, 63, 4.—According to experiments made in a German sole leather tannery with barbatimao bark in place of quebracho in connection with divi divi, myrabolams and valonia, a good tannage was obtained which gave a little redder color than quebracho, but showed no noticeable difference. An analysis of the bark showed 28 per cent. of tannin. The tannin easily penetrates into the skin and gives the leather a good and compact consistency.

**The Estimation of Lactic Acid in Lactic Acid Salts.** J. PAESSLER. *Collegium*, 1907, 282, 283, 388, 396.—The author gives a new method for the determination of lactic acid in lactic acid salts which consists in completely

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oxidizing the lactic acid in presence of sulphuric acid with a known amount of potassium bichromate in excess and then titrating the remaining bichromate in the usual way with potassium iodide and thiosulphate solution. The method is only applicable in the absence of other substances which act reducing on chromic acid, and is carried out by accurately weighing out an amount (about .4 gram) of the substance to be tested, or an aliquot portion of a known solution and placing the same in an Erlenmeyer flask with the addition of water, if necessary, and adding 10 cc. of dilute sulphuric acid (1: 10) and 25 cc. of N/2 potassium bichromate solution and boiling mildly for one hour, using a tube condenser. The excess of potassium bichromate is then titrated with N/10 thiosulphate solution, using 10 cc. of potassium iodide solution (1: 10) and a few drops of starch solution. Each cubic centimeter of N/2 potassium bichromate solution used in the oxidation is equal to .01127 gram of pure lactic acid. In case no thiosulphate is used up it indicates that not enough potassium bichromate was added and the test should be repeated with a larger amount.

## PATENTS

**Hide Working Machine, U. S. Patent No. 872,489,** to A. E. WHITNEY Winchester, Mass.—An improved bed-roll for hide working machines, consisting of a metal shaft covered with a thickness of soft spongy rubber, and an outer covering of a thickness of hard close-grained rubber.

**Scouring Machine: U. S. Patent No. 872,823,** to E. KETZLER, Chicago, Ill. —A scouring machine having two revolving brushes located one above the other, so that both sides of the goods are simultaneously worked.

**Tanning of Hides Previously Fitted upon Moulds or Frames:** H. BOULANGER, French Patent No. 378,103. —Skins, with or without hair, may be fixed upon frames or moulds and tanned, thereafter maintaining this form so produced.

**Process of Treating the Surface of Leather in Order to Render it Capable of Taking up Color:** H. NEUMANN, German Patent No. 178,016.—The leather is covered with zinc dust and then treated with an alkali sulphite solution. After rinsing, it is either exposed to the air or dipped into a weak acid solution to destroy the yellow color caused by the sulphite. After working, it is treated with a hot concentrated solution of sulphite, and again washed.

**Process for Tanning Hides and Skins:** A. WEINSCHENK, Mainz, Germany, English Patent No. 4,605.—Hides and skins may be tanned with naphthols if they are first prepared with an aldehyde of the aliphatic or aromatic series. They may also be first saturated with naphthol, and then with a further addition of the reagent, treated with aldehyde, or the two reagents may be made into a paste with water and gradually added to the hides suspended in water at 30–35° C. and kept in motion.

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## NOTES

*Tannic Acid.*—There is a large quantity of tannin bark made in Bône (Algeria), and Mr. Vice-Consul Scratchley suggests (Cd. 3727–18) that it might be advantageous to treat the bark so as to extract the tannic acid, and to ship it in the form of extract, instead of sending it away in its natural state. The tannin bark from the cork-wood tree contains about 12 per cent. of acid, but that of the green oak has only 6–7 per cent. If the tannic acid were extracted, a great gain would result in the bulk of the matter shipped. The leaves of the lentisk, or mastic bush, which cover an immense area in the forests, could also, the Vice-Consul says, be treated by the same process. The leaf is sometimes sent away under the name of sumach, which it somewhat resembles. Cork-wood waste having fallen considerably in value, the Vice-Consul suggests that it might be a profitable undertaking to reduce it to a powder and ship it in pressed bales. The powder is much easier to press than the bits of cork of different forms and sizes. As the waste in bags makes a very bulky parcel for little weight, shippers do not care to stow it in the hold unless the freight is high, and the buyers do not like waste to be shipped as a deck cargo.—*Journal of the Society of Arts.*

*Famine in Tan Bark Oak.*—A famine in tan bark oak is seriously threatening the Pacific Coast tanning industry. The continual harvesting of this oak is rapidly depleting the supply, and disastrous fires in the last fifteen years have destroyed bark which at present prices would be worth, it is estimated, one and one-third million dollars. The Pacific Coast tanning industry has always depended upon the native oak for tan bark. This oak is sprouting from the cut stumps, and if it were not for this quality the supply would probably have been exhausted years ago.—*Forestry and Irrigation.*

*Philippine Tannin Extract.*—The Bureau of Forestry in the Philippine Islands reports great commercial possibilities in the manufacture of tannin extract for export. It is probable few people know that the ordinary tan-barks used in the Philippines contain from 12–30 per cent. of tannin, being much stronger than oak or hemlock bark.

The Philippine tan-barks are gathered in the mangrove or tidal swamps common along the coast, especially at the mouths of rivers. Some of these swamps are very large, ten to twenty-five square miles in area. Nearly all of the trees in the swamps yield tan-bark, the best coming from the trees commonly known as bacao and tangal.

The United States imports an increasing amount every year of mangrove tan-bark from Africa. The reports of the U. S. Forest Service show that the home supply of tan-barks is decreasing rapidly and that the demand is increasing. Progressive American tanners are turning their attention to tropical tanning material. The Philippine Bureau of Forestry has received several inquiries during the past year from firms in the United States regarding Philippine tan-barks. It seems, however, that the high freight rates will make it impracticable to ship the crude bark to New York.

The only plant for the manufacture of cutch or mangrove tannin extract is operating very successfully in Sandakan, British North Borneo. A part of this company's output goes to New York.

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The Scotch firm who manufacture for such work estimate that the net profits of a plant large enough to produce five tons of solid extract per day should be over $44,000 per year; while the cost of the machinery, in Scotland, would be about $22,500.

The Philippines, with large areas of mangrove swamps and a fairly abundant labor supply, should be a very satisfactory field for such an enterprise.—*Forestry and Irrigation.*

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## THE SEYMOUR-JONES PRIZE

Mr. A. Seymour-Jones, the donor of the Seymour-Jones Prize, which consists of a silver medal for merit, and £10, has nominated Prof. Meunier, Dr. J. Gordon Parker and Mr. H. C. Reed, to act as judges and to award the Seymour-Jones Prize at the next Brussels Conference. The award is given for the best research work published in the *Collegium* or in the JOURNAL OF THE AMERICAN LEATHER CHEMISTS ASSOCIATION, since the Frankfort Conference.

## THE STANDARDIZATION OF HIDE-POWDER FOR TANNIN ANALYSIS. A REPLY

*By H. Garner Bennett, M.Sc.*

Some recent articles on this question, especially the report of the Committee of the A. L. C. A. on the Acidity of Hide-Powder,

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(J. A. L. C. A., II, 347), and the paper by H. C. Reed (J. A. L. C. A., II, 426) contain criticisms of the proposals of the author *re* a "Standard Hide-powder" (*J. S. C. I.*, **1907**, 455), and of the basic chloride method of tannin analysis elaborated by Professor Procter and the author (*J. S. C. I.*, **1906**, 1203, and **1907**, 79), which is now the official method of the I. A. L. T. C., and hence induce the writer to place before the American leather chemists some further experiments and conclusions, which are not contained in the author's previous publications but which have considerable bearing on the matter.

The chief point of discussion is the influence of the acidity of the hide-powder on non-tannin results, and as previously pointed out by the author the "total acidity" of the powder may be divided into two chief factors, that due to acid originally in the powder and that due to chroming; these will therefore be discussed separately.

### (1) *Original Acidity of the Hide-Powder*

With regard first of all to the method of estimating this, the writer would like to say that he read the report of the A. L. C. A. Committee with considerable astonishment. The statement that with the author's method "it was found difficult to satisfactorily duplicate results" is clear evidence that the method was not carried out as prescribed, but that the reading was taken before the titration was complete, and before a permanent pink was obtained. This is further proved by the results obtained, which are described as "too low," and is indeed admitted later in the report and advanced as the reason for the low results. The writer feels that it should be unnecessary to state to an association of chemists, that no method could be regarded as tested when used in such a manner, or rejected on such slender and unjustifiable evidence. The writer is even more astonished at the alternative method proposed by the committee. In ordinary volumetric analysis, who would think of adding a quantity of alkali more than eight times the equivalent of the acid it is desired indirectly to estimate? No wonder the committee found that the results were most concordant when a powder of low acid content was being tested, and that the results were constant "regardless of the amount of added alkali *provided it be in fair excess.*" If the principle of this modification of the author's method were

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correct, surely it should be possible to obtain equally concordant results and a greater accuracy, by using a small excess of alkali. Furthermore, the experiments showing the influence of the time of standing show clearly that the proper end-point is not really being obtained, and that the apparent concordance is an utter delusion. It seems curious that the committee did not test their method allowing the digestion to take place for more than the time they recommend. It is abundantly clear that this modification does not overcome the real difficulty—the obtaining of the end-point quickly—but merely covers up the defect, and the half hour's digestion previous to titration surely counterbalances any imaginary difference in the rates of diffusion of acids and alkalies. The fact is that the titration of acid or alkali in hide-powder cannot be done quickly, especially when near the neutral point, and the problem is not solved by introducing the necessity of two diffusions, *viz.*, first, of alkali to neutralize the acid, and second, of acid to neutralize the excess of alkali. The author would reiterate his view that if it is desirable to estimate the free acid in hide-powder at all, it should be done correctly, and the titration carried quite to the end, even if it is somewhat slow; and that if this be not done the percentage error on the true result is very large, especially when the acidity is small as in the I. A. L. T. C. powders. The writer has satisfied himself that his method, if carried out as prescribed, gives the correct result, and if the American chemists really wish for a different method he would suggest that they test it before adoption on a hide-powder purposely delimed with hydrochloric acid, and compare the results they obtain with those obtained by neutralizing with a slight excess of sodium carbonate, drying, ashing, dissolving up the ash, slightly acidifying with formic acid, neutralizing with a slight excess of magnesium oxide, and titration with $N/10AgNO_3$ in the presence of potassium chromate.

A more important matter is the effect that varying quantities of acid produce on the non-tannin determination, and the limits which should be specified for its variation. All are now agreed that there is such an effect and that the acidity of the unchromed powder should be defined, so that the author merely wishes to urge that the limits which he suggested in his previous paper, and which have been accepted by the I. A. L. T. C., *viz.*, less than 5.0 when determined by the direct titration of 6.5

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grams of dry powder, should be also accepted by the A. L. C. A. The committee of the latter admit in their report that such a powder is much more readily chromed, washed and squeezed, but suggest limits between 9.75 and 13.0, when expressed in terms of the Bennett method, and one member suggests that it should be definitely fixed at 11.7 by adjustment before chroming. This seems extraordinarily high, and may involve a considerable difference in the results obtained by European and American analyses. It must furthermore be borne in mind that some of this acid will undoubtedly be removed in the washing process, and it would hence be futile to fix the acidity at 11.7 or any other high figure if the quantity to be washed out is also not fixed. To estimate and control this during the washing would be excessively inconvenient, if not impossible, especially if the acidity due to chroming is to be simultaneously controlled. Another point is that our experiences with acid liquors, with acidified solutions of treated extracts (Parker and Bennett (*J. S. C. I.*, **1906**, p. 1193) and the observations of Reed (J. A. L. C. A., II, 426) all point to the undesirability of any appreciable quantities of free acids in solutions for evaporations, and hence point also to the desirability of a low acidity of hide-powder. The author has still no doubt that a higher acidity involves a higher absorption of non-tannins by hide-powder, and hence a more incorrect result, and his own work has been confirmed by Reed and others, though contradictory to the work of the A. L. C. A. Committee. This also, therefore, should be in favor of a low acidity of powder. A high acidity would also effect the basicity of a chroming solution, and consequently the degree of chroming. These difficulties are non-existent with a hide-powder of low acidity, and really point to the desirability of making the limit less than 5.0, though this is useful as a first limitation.

### (2) *Acidity Due to Chroming*

In the first place the writer is exceedingly pleased to note in H. C. Reed's paper some confirmations of the conclusions of Procter and Bennett that a more complete chroming is obtained in a shorter time by the use of basic chromium salts, especially with the use of a quantity of water only 10 times the weight of the hide-powder, and that it is desirable to fix the acidity due to chroming "so that it is not only definite, but of such a degree as

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to cause the lowest amount of absorption of non-tannin matters consistent with complete detannization." The writer is also glad that the method of Procter and Bennett of regulating the quantity of dry hide has also proved convenient to Mr. Reed (J. A. L. C. A., II, 328).

Really therefore the question is merely that of the most suitable acid radicle to which the chromium should be united in the material used for chroming hide-powder, and H. C. Reed suggests that a basic chromium formate might be considered as an alternative to basic chromium chloride. The importance of this matter was emphasized by Procter and Bennett in the elaboration of the basic chloride method, but the general conception of the "acidity" due to this source seems to be distinctly vague. In washing a freshly chromed hide-powder the following distinct functions are fulfilled:

(*a*) The powder is free from any unabsorbed chromic salt.

(*b*) The powder is washed free from potassium sulphate, sodium chloride, sodium formate, etc., which may be present, but not essentially required in the chroming process.

(*c*) The true chemical action of the water in producing a hydrolysis of the basic chrome salt combined with the fibre.

The extent of this hydrolysis is in all cases very small but continuous, an equilibrium being established with the basic chrome salt on the fibre, and the particular wash water with which it is in contact. The reduction in the amount of this hydrolysis by continued washing is very slight after the first few washings and is almost inappreciable by ordinary methods of analysis. Hence when the basicity of a chroming liquor is definitely prescribed and such as to render the powder insoluble, there is no reason to wash the hide-powder at all except to remove the unabsorbed chrome salts and the sodium chloride, potassium sulphate, etc., which may happen to be associated with the chroming material, and the American Leather Chemists will forgive the author pointing out that in their officially prescribed process of washing, the hide-powder is not freed from sulphates, for he cannot believe that any one continues to wash until the chrome salt is completely hydrolyzed, and no acid radicle at all is left in the hide-powder. In practice the process involves only the removal of the potassium sulphate present and the unabsorbed chromium sulphate, the absence of any

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further quantity of which is roughly tested by the addition of $BaCl_2$ to the wash liquor. The $SO_4$ radicle is not eliminated completely from the hide-powder, but can be continuously removed to a small extent by further washing. This can easily be demonstrated experimentally by conducting the test very carefully and allowing the mixture to stand for some time.

Hence also in the basic chloride method the aim of the washing process is merely to remove the sodium chloride which exists in the chroming material as a result of rendering the normal chloride basic,

$$Cr_2Cl_6 + 3NaOH = Cr_2(OH)_3Cl_3 + 3NaCl,$$

and any unabsorbed basic chromium chloride. When these salts are removed the powder may be considered "washed," for any further washing results in the reestablishment of the slight hydrolytic equilibrium previously mentioned. This equilibrium is of two types.

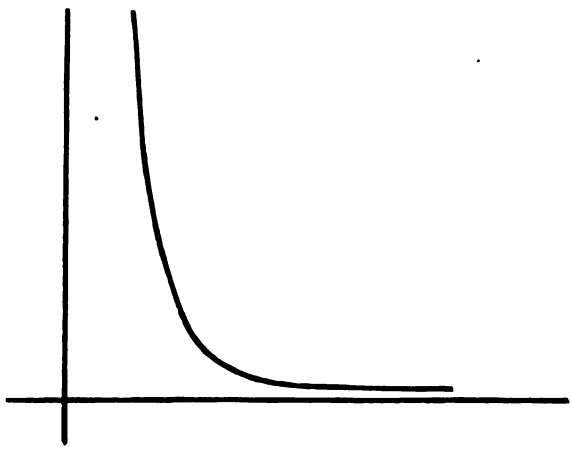
(1) The hydrolysis of the basic chromium chloride attached to the fibre into a still more basic chloride which still remains attached to the hide-powder, and a less basic chloride which goes into solution:

$$e.\ g.,\ 2Cr_2(OH)_3Cl_3 \rightleftharpoons Cr_2(OH)_4Cl_2 + Cr_2(OH)_2Cl_4$$

and (2), to a lesser extent, the further hydrolysis of this less basic soluble salt, thus:

$$Cr_2(OH)_2Cl_4 + H_2O \rightleftharpoons Cr_2(OH)_3Cl_3 + HCl.$$

With the basic chloride method the course of the washing process can be readily followed, and the reduction of total chlorides produces, as would be expected, a curve such as in the following diagram, which is actually the result of an experiment:



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Thus the aim of the washing process should be to reach the point where the curve is no longer steep, but becomes asymptotic, and this is the point at which the washing is ceased in the basic chloride method.

From these considerations it is clear that if a powder were sufficiently heavily chromed as to yield no soluble matter, with a basic chrome chloride which contains no free sodium chloride and which is completely absorbed by the fibre, the amount of washing required would be at a minimum. Procter and Bennett, however, found that such a solution was not readily prepared of sufficient basicity to accomplish this, and hence for the general convenience prescribed a solution of normal chloride made basic by adding alkali, and a definite ridding of the superfluous chlorides in the washing process. Similarly the A. L. C. A. may get rid of the "sulphate factor" by using a pure chromium sulphate rendered sufficiently basic by dissolving in it pure freshly precipitated $Cr_2(OH)_6$, but this will not prove easy or convenient.

As therefore we are practically compelled to use a chroming material containing neutral salts, it is clear that the material should be so chosen as to give the most convenient salt to estimate quickly, and the advantages of chlorides over sulphates, formates, etc., are surely obvious.

The titration of wash liquors with caustic soda, as in the experiments of Reed, seems to have little value, and certainly is no evidence of the rate at which sodium formate is being washed out of the powder. The figures obtained appear to show that appreciable amounts of a chromium formate are also washed out, and that this is the cause of the neutralization of the added alkali. Such a titration with caustic soda does not estimate "free" acid, but the acid actually combined with chromium, and under appropriate conditions forms the readiest method of determining the basicity of a chrome liquor (Proctor and McCandlish, J. S. C. I., **1907**, 458).

Another point is the impracticability of any prescribed mode of washing (such as suggested by Reed for formate) being of general applicability, unless it involve a considerable number of "squeezings," for the washing free from chlorides, etc., is merely due to repeated dilution, and is therefore largely dependent upon the extent of the pressure used in squeezing. The variation in form of the steep part of the curve is perhaps well illustrated by the

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following four experiments, in each of which the same minimum was eventually obtained. The figures represent cubic centimeters of N/10 $AgNO_3$ required by 50 cc. from each squeezing.

| | 1. | 2. | 3. | 4. |
|---|---|---|---|---|
| First squeezing | 8.6 | 9.9 | 9.85 | 8.7 |
| Second squeezing | 1.85 | 1.55 | 0.82 | 0.3 |
| Third squeezing | 0.6 | 0.45 | 0.45 | 0.3 |
| Fourth squeezing | 0.3 | 0.2 | 0.3 | 0.2 |
| Fifth squeezing | 0.2 | 0.2 | 0.2 | 0.2 |
| Sixth squeezing | 0.2 | — | 0.2 | — |

The author can endorse the experiences of Reed that troubles arise by washing any chromed powder with impure waters, and it would seem therefore that the most scientific, most rapid, and most economical way to wash powder is to use distilled water only and a mechanical press. The difficulties of Reed in obtaining a satisfactory chromium formate can also be confirmed by the writer, who also observed that the salt when finally obtained in a crystalline condition does not keep well, but breaks up into what is apparently an insoluble basic salt and a soluble acid salt, and it should perhaps be mentioned that the use of chromium formate for the purpose hide-powder was very carefully considered and experimentally tested by Procter and Bennett before their work on chromium chloride, but was rejected on the grounds given in the paper.

A point raised by Reed is the possible effect of free acids formed by hydrolysis on the non-tanning substances during the evaporation and drying. But should it not be shown first that these free acids (HCl, $H_2SO_4$, HCOOH, etc.) really do exist in the free state in the non-tan filtrates obtained in the ordinary course of analysis? This Reed assumes on the basis of a statement by Procter and Bennett that of the chlorides found in non-tan filtrates "some portions at least....are volatile, and are in all probability free acid." The author desires to state therefore that further experiments have shown that the occurrence of such volatile portions is unusual, and that as a rule the titration of 50 cc. non-tan filtrate with N/10 $AgNO_3$ gives the same result as the titration of the redissolved non-tan residue evaporated to dryness from 50 cc. of the same solution, and that in no case has the difference in such titrations been greater than 0.05 cc. and hence almost within the error of experimental determination.

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Even if the hydrolysis of the chrome salt in the powder were at its maximum, *viz.*, when 50 cc. require 0.2 cc. N/10 $AgNO_3$, and this were all "free" acid the author would never expect this to occur as free acid in the non-tan filtrates, for practically all extracts and tanning materials contain quantities of metallic tannates and other alkaline salts which are quite sufficient to cause the complete neutralization of any free acid of this order of quantity, so that Reed's experiments on the effect of free hydrochloric acid on the non-tannin residues, though interesting, are scarcely evidence against the basic chloride method. The fact that no free hydrochloric acid exists in ordinary non-tan filtrates obtained with the use of the basic chloride method is further proved by the absence of any difficulties with European chemists due to difficultly soluble residues, "caramel odors," etc. It is conceivable that this difficulty might occur if a greater percentage of chromic chloride and a less basicity were used, but this possibility was borne in mind by Procter and Bennett and its occurrence guarded against.

Reed's experiments have, however, considerable interest in other ways, for in the analysis of tannery liquors the presence of free acids is beyond doubt and hitherto beyond elimination. In this case the observations as to the effect of free acids may have some force, though in liquors which contain naturally ionized chlorides, sulphates, acetates, lactates, etc., as well as free acids, it would seem impossible to state which free acid is having its specific effect, and to what extent. The justifiable conclusion from Reed's figures is the desirability of a process of rapid evaporation and drying, and the undesirability of such a machine as the combined evaporator and drier in which the evaporation is protracted over a period of five hours, and the drying continued for another twelve hours, thereby giving every possible chance to inversion, caramelization, oxidation, etc.

In conclusion the author would ask his American colleagues to consider the revision of their method of chroming hide-powder not only without prejudice, but also with regard to general convenience, and the unification of European and American practice. If this be done the writer has no doubt that the advantages of only one hour's chroming, of greater insolubility of powder, of a definite "acidity" due to chroming, which is capable of easy and accurate control, of definite acidity and texture of original hide-

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powder, will all tend to the view that it would be best to adopt the I. A. L. T. C. method as it stands. The European Association in abolishing the filter bell and adopting an agitation method, have proved their willingness to meet their American colleagues in methods where increased accuracy and convenience has been demonstrated, so that if there is any reality in the right hand of good fellowship so long held out in Europe, would not this be a suitable matter and occasion to demonstrate it?

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## PROVISIONAL METHODS FOR THE ANALYSIS OF OILS AND FATS

### *Saponification Value*

*Preparation of the Alcoholic KOH.*—Purify the alcohol as follows: To ordinary alcohol add potassium permanganate in very fine powder or saturated solution until the pink color holds for about ten minutes; allow to stand over night, filter and distil over a fixed oil and sodium hydroxide, the first portions of the distillate, about a quarter, being rejected. Dissolve the KOH in the alcohol thus prepared, filter, and make up to half-normal strength.

*Determination.*—Weigh off accurately in a flask holding 150–200 cc., 1.5–2.0 grams of the fat, or oil, purified and filtered if necessary. Next run into the flask 25 cc. of the alcoholic potash, attach a long cooling tube or invert condenser, and heat on the water bath for thirty minutes, frequently imparting a rotary motion to the contents of the flask until complete solution has been effected, which can always be done unless there is considerable unsaponifiable material present. After this allow to simmer, but not to boil vigorously, for the remainder of the time. Next add 1 cc. of a 1 per cent. phenolphthalein solution (prepared by dissolving 1 gram phenolphthalein in 100 cc. 90 per cent. alcohol) and titrate back the excess of potash with half-normal hydrochloric acid.

It is always best to make a blank test, treating the same amount of alcoholic potash in exactly the same manner as the solution of fat. Every source of error, as carbonic acid, etc., has therefore, as nearly as possible, the same influence on the final result, and is thus eliminated. The difference in the number of cubic centimeters of acid used for the blank test and the real test corresponds

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to the quantity of potash required, and is calculated to milligrams of potash to 1 gram of fat.

*Acid Value*

Weigh accurately a convenient quantity of the material to be tested into an Erlenmeyer flask, and treat with about 25 cc. of a mixture of alcohol and ether, previously rendered slightly pink with alcoholic KOH after the addition of 1 cc. 1 per cent. phenolphthalein solution. Then titrate the mixture to the same point to which the solvent had been brought. Use tenth-normal alcoholic KOH for this and from the number of cubic centimeters required, calculate the amount of KOH absorbed. This expressed as the number of milligrams per gram of substance is the acid value.

*Iodine Value*

A. O. A. C. Official Method—The Hanus Method
Bulletin No. 107
(*a*) Preparation of Reagents

*Hanus Iodine Solution.*—Dissolve 13.2 grams of iodine in 1000 cc. of glacial acetic acid (99.5 per cent.) showing no reduction with bichromate and sulphuric acid; add enough bromine to double the halogen content determined by titration—3 cc. of bromine is about the proper amount. The iodine may be dissolved by the aid of heat, but the solution should be cold when bromine is added.

*Decinormal Sodium Thiosulphate Solution.*—Dissolve 24.8 grams of chemically pure thiosulphate, freshly pulverized as finely as possible and dried between filter- or blotting-paper, and dilute with water to 1 liter at the temperature at which the titrations are to be made.

*Starch Paste.*—Boil 1 gram of starch in 200 cc. of distilled water for ten minutes and cool to room temperature.

*Solution of Potassium Iodide.*—Dissolve 150 grams of potassium iodide in water and make up 1 liter.

*Decinormal Potassium Bichromate.*—Dissolve 4.9083 grams of chemically pure potassium bichromate in distilled water and make the volume up to 1 liter at the temperature at which the titrations are to be made. The bichromate solution should be checked against pure iron.

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(*b*) Determination

(*1*) *Standardizing the Sodium Thiosulphate Solution.*—Place 20 cc. of the potassium bichromate solution, to which has been added 10 cc. of the solution of potassium iodide in a glass-stoppered flask. Add to this 5 cc. of strong hydrochloric acid. Allow the solution of sodium thiosulphate to flow slowly into the flask until the yellow color of the liquid has almost disappeared. Add a few drops of the starch paste, and with constant shaking continue to add the sodium thiosulphate solution until the blue color just disappears.

(*2*) *Weighing the Sample.*—Weigh about 0.5 gram of fat or 0.250 gram of oil[1] on a small watch crystal or in some other suitable way. Melt the fat, mix thoroughly, pour onto the crystal and allow to cool. Introduce the watch crystal into a wide mouth 16-ounce bottle with ground-glass stopper.

(*3*) *Absorption of Iodine in Hanus Method.*—Add 25 cc. of the iodine solution to the fat or oil dissolved in 10 cc. of chloroform. Allow to stand, with occasional shaking, for thirty minutes. The excess of iodine should be at least 60 per cent. of the amount added.

(*4*) *Titration of the Unabsorbed Iodine.*—Add 10 cc. of the potassium iodide solution and shake thoroughly, then add 100 cc. of distilled water to the contents of the bottle, washing down any free iodine that may be noted on the stopper. Titrate the iodine with the sodium thiosulphate solution, which is added gradually, with constant shaking, until the yellow color of the solution has almost disappeared. Add a few drops of starch paste and continue the titration until the blue color has entirely disappeared. Toward the end of the reaction, stopper the bottle and shake violently, so that any iodine remaining in solution in the chloroform may be taken up by the potassium iodide solution.

(5) *Standardizing the Iodine Solution by Thiosulphate Solution.*—At the time of adding the iodine solution to the fat employ two bottles of the same size as those used for the determination for conducting the operation described under paragraphs (3), (4) and (5), but without the presence of any fat. In every other respect the performance of the blank experiments should be just

[1] Use from 0.100 to 0.200 gram in case of drying oils which have a very high absorbent power.

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as described. These blank experiments must be made each time the iodine solution is used. Great care must be taken that the temperature of the solution does not change during the time of the operation, as acetic acid and alcohol have very high coefficients of expansion, and a slight change of temperature makes an appreciable difference in the strength of the solution.

Per cent. of iodine absorbed:

| | | |
|---|---|---|
| Weight of fat taken | 1.0479 | grams |
| Quantity of iodine solution used | 40.0 | cc. |
| Thiosulphate equivalent to iodine used | 62.1 | cc. |
| Thiosulphate equivalent to remaining iodine | 30.2 | cc. |
| Thiosulphate equivalent to iodine absorbed | 31.9 | cc. |
| Per cent. of iodine absorbed (31.9 × 0.012697 × 100) divided by 1.0479 | 38.65 | |

*Unsaponifiable Matter*

Wherever possible use the following method: Saponify 5 grams, or its equivalent, with 5 cc. of a 50 per cent. by volume aqueous KOH solution and 25 cc. alcohol. Heat on the water bath for half an hour, frequently agitating at the beginning until as complete solution has been effected as is possible. Then transfer to a shallow porcelain dish, using alcohol to rinse the flask. When the alcohol is about half evaporated off, mix 10 grams of sodium bicarbonate and 25 grams of clean quartz sand, previously washed with HCl and distilled water and dried thoroughly. Add this mixture to the soap and stir together with a glass rod. Evaporate to dryness and continue the drying for several hours or over night. The mixture is then pulverized and placed in a Soxhlet extraction apparatus, where it is extracted with a low-boiling petroleum ether for four or five hours. The other solution, containing the unsaponifiable matter is then transferred to a separatory funnel and washed with distilled water. Then filter into a tared flask, and distil off the solvent. The last traces may be removed by passing a current of air through the flask over the residue and finally drying in an oven at 98–100° C. for four hours. The residue is weighed as unsaponifiable matter.

For oils that can not be treated in this way on account of their forming a glutinous mass with petroleum ether, proceed as follows:

Saponify in the same manner as above and transfer to a shallow porcelain dish. Evaporate to dryness and continue to dry for

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several hours, or over night, but without adding sand and sodium bicarbonate. Next add about 30 cc. petroleum ether and rub it up with the soap by means of a glass rod flattened at one end. Then decant off the ether, with whatever soap may be in suspension in a finely divided condition and repeat the operation several times until the soap is thoroughly extracted. No less than 200 or 300 cc. in all should be used. The soap in suspension, as well as in solution is next washed out with distilled water in a separatory funnel, using a little alcohol to break up emulsions. The washing should be proceeded with cautiously at first, and the clear ether transferred to another funnel as fast as it is formed where it may be vigorously shaken. The aqueous soap solution should also be shaken out with petroleum ether as some of the unsaponifiable matter is apt to pass into the aqueous part together with the soap. When thoroughly washed, all the ether solutions are filtered into a tared flask, the solvent distilled off, the last traces being removed by passing a current of air through the flask and drying in the oven for four hours, as above. The residue, however, may contain small amounts of fatty acids which can be determined from the acidity and a correction made.

*Maumené Test*

In a tall 100 cc. beaker weigh out such a quantity of oil as when made up to 50 grams with mineral oil will not give a rise in temperature above 60° C. Make up to 50 grams with mineral oil and place in a large beaker well lined with hair. Add 10 cc. concentrated sulphuric acid of the same temperature as the oil mixture, taking one minute to add and always allowing the pipette to drain the same length of time. Stir constantly with the thermometer during the addition of acid and continue stirring until the temperature has reached the highest point. Run blank, using the same amount of mineral as for test. Deduct this rise from the total rise for the mixed oil. For specific temperature, run 50 grams of water in the same way as the sample was run. Divide the rise in temperature per gram of oil by rise in temperature per gram of water and multiply the result by 100.

*Specific Gravity*

Specific gravity should be determined at 20° C., both the substance and the distilled water with which it is compared being at that temperature.

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*Titer Test—Provisional*

A. O. A. C. Provisional Method

Bulletin No. 107

(*a*) Standard Thermometer

The thermometer must be graduated in tenth degrees from 10° to 60°, with a zero mark, and have an auxiliary reservoir at the upper end, also one between the zero mark and the 10° mark. The cavity in the capillary tube between the zero mark and the 10° mark must be at least 1 cm. below the 10° mark, the 10° mark to be about 3 or 4 cm. above the bulb, the length of the thermometer being about fifteen inches over all. The thermometer is annealed for seventy-five hours at 450° C. and the bulb is of Jena normal 16-inch glass, moderately thin, so that the thermometer will be quick-acting. The bulb is about 3 cm. long and 6 mm. in diameter. The stem of the thermometer is 6 mm. in diameter and made of the best thermometer tubing, with scale etched on the stem, the graduation to be clear cut and distinct but quite fine.

(*b*) Determination

Saponify 75 grams of fat in a metal dish with 60 cc. of 30 per cent. sodium hydroxide (36° Baumé) and 75 cc. of 95 per cent. by volume alcohol or 120 cc. of water. Boil to dryness, with constant stirring to prevent scorching, over a very low flame or over an iron or asbestos plate. Dissolve the dry soap in a liter of boiling water, and if alcohol has been used boil for forty minutes in order to remove it, adding sufficient water to replace that lost in boiling. Add 100 cc. of 30 per cent. sulphuric acid (25° Baumé) to free the fatty acids and boil until they form a clear, transparent layer. Wash with boiling water until free from sulphuric acid, collect in a small beaker, and place on the steam bath until the water has settled and the fatty acids are clear; then decant them into a dry beaker, filter, using hot water funnel, and dry twenty minutes at 100° C. When dried, cool the fatty acids to 15° or 20° C. above the expected titer and transfer to the titer tube, which is 25 mm. in diameter and 100 mm. in length (1 × 4 inches) and made of glass about 1 mm. in thickness. Place in a 16-ounce saltmouth bottle of clear glass, about 70 mm. in diameter and 150 mm. high (2.8 × 6 inches), fit it with a cork, which is perforated so as to hold the tube rigidly when in position. Sus-

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pend the thermometer, graduated to 0.10° C., so that it can be used as a stirrer, and stir the mass slowly until the mercury remains stationary for thirty seconds. Then allow the thermometer to hang quietly, with the bulb in the center of the mass, and observe the rise of the mercury. The highest point to which it rises is recorded as the titer of the fatty acids.

Test the fatty acids for complete saponification as follows:

Place 3 cc. in a test tube and add 15 cc. of alcohol (95 per cent. by volume). Bring the mixture to a boil and add an equal volume of ammonium hydroxide (0.96 sp. gr.). A clear solution should result, turbidity indicating unsaponified fat. The titer must be made at about 20° C. for all fats having a titer above 30° C. and at 10° C. below the titer for all other fats.

### *Melting-Point*

Take a tube of thin glass 2½ inches in length, and of such size that when the thermometer is inserted there will be about 1 mm. space between it and the glass. Fuse one end of the tube in the flame until the edges are drawn in slightly, forming a smooth, round hole. About half an inch from the other end make a small hole, either by fusing and blowing, or by filing. The tube is then ready for use. Draw a rubber band tightly over the end that was partially closed by fusion and bind on with a rubber ring. Pour such a quantity of the melted fat into the tube that when the thermometer is inserted the bulb will be a little more than covered by fat. The column of fat should then be about one and one-fourth inch in height. The thermometer, which is inserted to near the bottom of the tube is firmly secured with a perforated cork. The fat is now cooled well down below its melting-point by immersing in cold water. When this is done, take the apparatus from the cold water, remove the rubber band, and wipe dry. Then suspend the thermometer with the tube and fat attached, in an Erlenmeyer flask, or other convenient air bath, securing it by means of a cork. Place on a water bath and as the temperature slowly rises note the point at which the fat begins to protrude quite perceptibly, also the point at which the first drop falls and the point at which the fat becomes clear. For the latter, a small cork is inserted to prevent the fat from running out. Then remove the cork, and as the fat runs out notice its consistency, whether thin or viscous.

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*Cold Test—Millwood*

Warm the oil until the stearine is dissolved and filter, through several thicknesses of filter paper, into a *dry* 4-ounce wide-mouth bottle, 1½ ounces of the oil to be tested; place in a freezing mixture and stir until the oil becomes solid, then cork and leave for one hour in the freezing mixture. Take the bottle from the freezing mixture, wipe it dry, and place in a holder of ordinary magnesia, asbestos pipe covering, or any suitable holder which will insulate the sides of the bottle. The frozen oil is broken up and well stirred with the thermometer, and at every degree rise in the temperature the bottle is inverted; continue until the oil will run to the other end of the bottle. The temperature registered at this stage is to be considered the cold test.

*Cloud Test—Manns*

(1) The oil must be perfectly dry, because the presence of moisture will produce a turbidity before the clouding point is reached.

(2) The oil must be heated to 150° C. over a free flame, immediately before making the test.

(3) There must not be too much discrepancy between the temperature of the bath and the clouding point of the oil. An oil that will cloud at the temperature of hydrant water should be tested in bath of that temperature. An oil that will cloud in a mixture of ice and water should be tested in such a bath. An oil that will not cloud in a bath of ice and water must be tested in a bath of salt, ice and water. The test is conducted as follows: the oil is heated in a porcelain casserole over a free flame to 150° C., stirring with the thermometer. As soon as it can be done with safety, the oil is transferred to a 4-ounce bottle, which must be perfectly dry. One and one-half ounces of the oil are sufficient for the test. A dry Fahrenheit thermometer is placed in the oil, and the bottle is then cooled in a suitable bath. The oil is constantly stirred with the thermometer, taking care not to remove the thermometer from the oil at any time during the test, so as to avoid stirring air bubbles into the oil. The bottle is frequently removed from the bath for a few minutes. The oil must not be allowed to chill on the sides and bottom of the bottle. This is effected by constant and vigorous stirring with the thermometer.

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As soon as the first permanent cloud shows in the dry body of the oil, the temperature at which this cloud occurs is noted.

With care, results concordant to within 1 degree Fahrenheit can be obtained by this method. The Fahrenheit thermometer is used merely because it has become customary to report results in degrees Fahrenheit. The oil must be tested within a short time after heating to 150° C., and a re-test must always be preceded by reheating to that temperature. The cloud point should be approached as quickly as possible, yet not so fast that the oil is frozen on the sides or bottom of the bottle before the cloud test is reached.

## A REPLY TO MR. EARP

*By H. C. Reed*

The January (1908) issue of this Journal contains a reply from Mr. Earp to a criticism (Journal A. L. C. A., May, 1907) of his work upon the gelatine-salt test for tannin (*Collegium*, No. 253, 1907).

Mr. Earp concludes that the antagonistic results of the tests may lie (1) in the state of the gelatine and (2) in the strength of the acid.

As to the second possibility, the strength of the acid which gave the results alluded to was identical with that used by Mr. Earp; the ordinary concentrated diluted one in four. The gelatine was Nelson's photographic, the purest that could be gotten. In order to verify the tests, solutions of gallotannic acid and chestnut extract were made of the dilutions indicated in the original paper, and to 5 cc. of each, 10 cc. of gelatine-salt solution (1 per cent. gelatine, 10 per cent. salt) was added followed by 1 cc. hydrochloric acid (1 in 4) as directed by Mr. Earp. The results confirmed in every respect those already noted. Also, the addition of 1 cc. of a 1 per cent. solution of chrome alum was again found to intensify the delicacy of the test. The gelatine solutions used in this and following experiments were freshly made up for each day's work. Thus the results are comparable unless Mr. Earp's are based on conclusions drawn from reactions obtained with old gelatine solutions.

On the chance that differences might arise from variations in the character of the gelatines themselves, experiments were run

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with five other makes of gelatines: Knox's, Cooper's, Cox's, one of make unknown and a French gelatine. Gallotannic acid and chestnut extract solutions of strengths 1/7500, 1/30000 and 1/60000 were tested by Mr. Earp's method and by the official method. In no single instance did Mr. Earp's method give a definite, curdy precipitate, the opalescence shown in the tests being proportional to the strength of the tan solution. The results from the official method were, however, somewhat striking, and throw some light on variable results from the gelatine test. These are here tabulated:

GELATINE SALT TEST WITH VARIOUS GELATINES

(Gelatine 1 per cent., Salt 10 per cent.)

Gallotannic Acid and Chestnut Extract Solutions

| Gelatine. | Official. | Tan sol. acidified with very dilute acetic acid. | Tan sol. acidified stronger sol. acetic acid. | Acidity of gelatine sol. cc. N/10NaOH per 100 cc. | Strength of tan sol. |
|---|---|---|---|---|---|
| Nelson | Least delicate | Intensified | No test | .8 | 1/7500 |
| Knox | Most " | " | " | 6.0 | 1/7500 |
| Cooper | 4th in delicacy | " | " | 2.8 | 1/7500 |
| Cox | 5th " " | " | " | 1.0 | 1/7500 |
| Unknown | 2nd " " | " | " | 5.2 | 1/7500 |
| French | 3rd " " | " | " | 4.0 | 1/7500 |
| Nelson | Faint opalescence | Marked opalescence | " | — | 1/30000 |
| Knox | Marked " | " " | " | — | 1/30000 |
| Cooper | Faint " | " " | " | — | 1/30000 |
| Cox | " " | " " | " | — | 1/30000 |
| Unknown | Opalescent | " " | " | — | 1/30000 |
| French | " | " " | " | — | 1/30000 |
| Nelson | No test | " " | " | — | 1/60000 |
| Knox | Opalescent | " " | " | — | 1/60000 |
| Cooper | No test | " " | " | — | 1/60000 |
| Cox | " | " " | " | — | 1/60000 |
| Unknown | Opalescent | " " | " | — | 1/60000 |
| French | " | " " | " | — | 1/60000 |

Tests were made also to determine the effect of acidifying the gelatine-salt solutions themselves, and it was found that by so doing the delicacy of the reaction was intensified in exactly the same manner as by acidifying the tan solutions. It is evident from the tables that we are again confronted with the necessity of a strict holding to an empirical method if we expect to obtain

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anything approaching agreement, as the delicacy of the test is directly dependent upon the acidity of the test solution as well as the acidity of the tan solution. Past discrepancies are neither difficult of explanation nor to be wondered at.

Mr. Earp asks whether a mixture of 5 cc. water, 10 cc. gelatine solution and 1 cc. dilute hydrochloric acid precipitated when two or yet five drops more of the diluted acid were added. Not one of the six gelatine solutions so behaved. One or two drops of the acid produced a precipitate dissolving to a solution slightly intensified in opalescence when the acid was added up to 1 cc.; further additions of acid, even in considerable quantity, failed utterly to produce a precipitate. It would appear that Mr. Earp's gelatine-salt solution must have been in a peculiar and unusual condition to have given the precipitation.

An effort was then made to produce a gelatine-salt solution that would comply with the conditions cited by Mr. Earp relative to precipitation with a slight excess of the diluted acid, but with negative results. It was found, however, that it was possible by increasing the percentage of salt to obtain a test solution that would by his method give a definite, curdy precipitate with dilute tan solutions, and that the amount of added salt varied with the different gelatines. Too much salt gave a solution which precipitated on adding a drop of the dilute hydrochloric, failing to dissolve in 1 cc. of the acid. For example, Nelson's gelatine 1 per cent., salt 15 per cent. gave a precipitate insoluble in 1 cc. of acid, while 1 per cent. of the same gelatine with 13.5 per cent. salt, precipitated with a few drops of the acid but gave no precipitation when as much as 1 cc. acid was present. To meet the latter conditions it required approximately for gelatine solutions of 1 per cent., 14.5 per cent. salt for Knox's, 16 per cent. for Cooper's, 14 per cent. for Cox's and 14.5 per cent. for the sample of unknown make.

Experiments were then conducted with these extra-salted gelatine solutions to ascertain the effect of the presence of chrome alum. It was found, as stated by Mr. Earp, that if 1 cc. of a 0.1 per cent. chrome alum solution is added precipitation is retarded, but it was further learned that this is due not to the fact of the presence of chrome alum but to the dilution of the tan solution by 1 cc. of the chrome alum solution. For example, 5 cc. of a 1/10000 solution of gallotannic acid gave a flocculent

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precipitate with an extra-salted gelatine solution by Mr. Earp's method of testing, and failed to give a precipitate in the presence of 1 cc. of chrome alum solution. When 3.75 cc. of a 1/7500 solution gallotannic acid (containing tan equal to 5 cc. of a 1/10000 solution) was made up to 5 cc. with 1 cc. chrome alum solution and 25 cc. water, the flocculent precipitate immediately appeared upon the addition of the 1 cc. hydrochloric acid after mixing with 10 cc. of the extra-salted gelatine solution.

Gallic acid even in quite dilute solution was found to give a precipitate of the same character as the tan under similar conditions. One cannot but be somewhat staggered by the bulk of the precipitate thus obtained in tan solutions so dilute, and to marvel at the tremendous proportion of gelatine that must be present in the tanno-gelatine precipitate. In a 1/60000 tan solution there is in 5 cc. .0000835 gram tan, to which is added 10 cc. of a solution containing .1 gram gelatine, or nearly twelve hundred times as much gelatine as tan, giving a bulky, flocculent precipitate which Mr. Earp calls a definite, curdy precipitate of tanno-gelatine. Acidification of a tan solution with a drop of dilute acid will, after the addition of one drop of the official gelatine solution, give an opalescence in a solution as dilute as 1 part of tan to 300,000 of water, and in a 1/60000 solution an opalescence showing an amount that might reasonably be expected in the presence of so little tan. It seems quite possible that the intensification of the official test in the presence of chrome alum is due to the acidity of the chrome alum.

Mr. Earp remarks that "it stands to reason that if even such a slight amount of a colloidal body like tan be added to another colloidal body like gelatine, just on the point of breaking up into insoluble form, the balance of solubility will be upset and the tan will form a precipitate.' But even with the additional salt no such precipitate formed until the hydrochloric acid is added. Are, then, neither tan solutions nor gelatine solutions colloidal without the presence of the acid?

The non-tan solution from a chestnut extract, detannized officially gave a flocculent precipitate with a solution of extra-salted gelatine by Mr. Earp's procedure. A portion of the non-tan solution shaken a second time with a fresh quantity of hide-powder still gave the test, and on a third detannization with fresh powder the precipitation was yet in evidence. The non-

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tan from a quebracho extract acidified with very dilute acetic acid and tested with the official gelatine-salt solution gave not a trace of opalescence. The same non-tan solution tested by Mr. Earp's method using extra-salted gelatine gave a flocculent precipitate.

I do not mean to infer that Mr. Earp used more than 10 per cent. of salt with his gelatine solution, but wish clearly to bring out that it was only by so doing that results akin to Mr. Earp's could be gotten. If Mr. Earp's gelatine solution at all corresponded with those employed in the experiments where additional salt was used, it is not to be wondered at that he remarks that "I am prepared to separate tan in any liquor so detannized in amount of the order of magnitude of what I have already indicated as being present in them."

Mr. Earp says "the amount of hide used in our old method is about ten times the amount required to produce a lightly tanned powder, and that in the new method about double as much." He makes no mention as to quantity of tan presented to hide, which is a constant by the new but not necessarily so by the old method. It is not quite clear how the amount of hide (to tan) is about double as much by the new method as by the old. Mr. Earp evidently grants a certain gain in uniformity by chroming.

It is contended that the statement made by Mr. Earp (*Collegium* No. 253, page 147) that "the process of absorption of tan or of non-tan is a reversible one" is open to the construction that the action of the absorption and reverse took place in one and the same system. As to the statement which Mr. Earp attributes to the author anent the superiority of the shake over the filter method (Journal A. L. C. A., **1907,** page 163) a reference to the text is sufficient to prove that he did not say that "fresh hide is continuously presented to the solution in the shake method." Mr. Earp believes in a method that presents fresh hide continuously to the solution, and in doing so evidently ignores the absorption of non-tans by hide or believes that such absorption does not take place. Admitting for the argument, that our method does not remove all the tan, and that we should use, as Mr. Earp suggests, a "double shake method," it will strike the majority of those who have taken sufficient interest in the point to make actual tests that the second shaking will show at least

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equal and probably considerably greater absorption of non-tan than tan. If Mr. Earp is able to work out the constants for use in estimating the residues of supposable tannin remaining in the non-tannin filtrates, it would seem that for the good of the cause he should delay no longer than necessary in doing so. Even if the supposition that tan remained in the filtrate were correct, it does not appear a reasonable presumption that even the solutions made from different extracts of the same tanning material would give the same constants; certainly not from different tanning materials.

In conclusion it would seem possible that the phenomenon by which Mr. Earp obtains a definite, curdy precipitate of tanno-gelatine, is due either to an acid-gelatine condition or to a condition of supersaturated solution, possibly to both. It is not possible for the author to believe that a precipitate of the bulk and character of that obtained is one of tanno-gelatine when tan is present in quantities so minute.

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## THE ADULTERATION OF BOOTS

*By Prof. H. R. Procter*

(An address given to the Federation of Boot Retailers' Associations in Liverpool.)

This subject falls under two heads, *viz.*:

The construction of boots of improper and concealed material.

The improper additions to material used by boot manufacturers.

It is, however, difficult to draw a clear line either between these heads, or, in both cases, between proper and improper material, but the essence of adulteration is that purchaser is deceived into buying something other than he purports to pay for. In some cases the injury is commercial only; it is clearly and legally adulteration to mix margarine or cocoanut fat with butter, since they are of lower commercial value, though quite wholesome, and perhaps equally nutritious. If the adulterated butter is sold, as is possible, at its commercial value, the purchaser suffers no real injury, but the vendor of a genuine butter suffers by the unfair competition. Applying the same rule to the boot question, the purchaser of a heavy boot with a straw-board sole suffers probably both in pocket and health by obtaining an

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article which even if sold at a fair cost value is not the article it appears to be, or which he requires for practical use, while the whole boot trade suffers by the unfair competition of the inferior article with honest and genuine manufacture, a difference which the buyer is unable to detect. The inevitable result of such imitation is to discredit not only the imitation, but the genuine article, and even to spoil the market for both. Genuine levant seal was at one time a favorite and really excellent material for boot uppers. It was imitated so closely in embossed calf that the public could not detect the difference, but the printed grain stretched out and disappeared in wear, and both imitation and genuine seal were discredited, and went out of fashion. The same is only too likely to prove true of genuine box calf, and its kip "semi-chrome" imitations. The public finds out the cheat in the long run, and neither forgives nor forgets, and the innocent suffer with the guilty. It may also be urged that, however the manufacturer may salve his conscience, the buyer never does get the imitation at its commercial value, since if he did there would be no more profit in the inferior than in the honest articles.

While the straw-board sole is alike a menace to the public and the honest boot trade, it is even more so to the useful leather substitutes, which, at the present price of leather, might be quite legitimately (if it could be honestly) used for many classes of goods. Leather substitutes are on the market which are quite equal in water resistance, and probably also in wear, to the inferior grades of sole leather; but their manufacturers tell me that the sales are small, since they cannot compete in price with straw-board, and the manufacturers who use such things at all will not buy any but the lowest priced. I need not repeat the same arguments with regard to uppers. Cloth uppers are quite legitimate if they can be sold, so are sheep and other cheaper leathers sold as such, but not if sold as glacé goat or box calf; but it is hard here to draw too sharp a line. Leather imitations for shoes need hardly be considered yet, however important in the purse, portfolio, and bag trades. Paper is too bad for the most jerry slipper maker, and anything else is too dear to compete with the cheaper leathers, as the imitation so far is hardly good enough to deceive even the average public into the idea that they are buying "solid leather!"

I will not, however, attempt to go into further detail on a side

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of the question on which I have no personal experience, but will turn from the question of whether or how certain manufacturers may cheat the public, to that (which no doubt will seem more interesting to the present company) of how the manufacturers may be cheated themselves.

So far I have spoken as if the question was solely one between the manufacturers and the public, but I must not forget that I am speaking to an association of boot retailers, who in one sense are "between the upper and the nether millstone," but who truly are probably the arbiters of the situation. Although I am, perhaps, hardly to be classed with the general public in my knowledge of leather, I regard my boot dealer as in a position of trust. I confess to him honestly that I cannot judge by appearance whether the material is good or bad, and I rely on him to give me honest value for the price I am able or willing to pay. I must admit that I seldom limit him as regards the last, and that so far I have had no cause to complain of his honesty, if I have now and then of his judgment. If, however, I were discontented I should probably, as I am a peace-loving man, say nothing, but go next time elsewhere; the boot dealer would have one customer less and would be ignorant of the cause, and on this point I take it I behave like the average public. Now an American philosopher has pointed out that though you can fool all men sometimes and some men all times, you cannot fool all men all times, and I believe on the whole the public does not like to be fooled and does not forget. The wise retailer aims to give his customer good value, but one cannot help thinking that if he had a little more courage in pointing out the better value of better stock he would build a sounder trade.

With regard to sole leathers, the most important considerations to the public are those of durability and of resistance to moisture, while to the manufacturer that of weight or cost of soles of a given thickness and apparent quality takes the first and often, I fear, the only place. In all these directions leather may be deteriorated by the addition of substances such as glucose and barium chloride, which every one must admit are adulterations, but I doubt if the effects of any direct adulteration are so serious as those of what may be considered legitimate methods of manufacture. The use of splits and pasted scrap for middle soles, if technically "solid leather," is probably not more advantageous to the public

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than that of the better forms of leather substitute of the nature of "vulcanized fibre," which may be made more waterproof and probably more durable for such a purpose than leather itself. Without professing an expert knowledge, I am inclined to think that a high-class boot would often be really improved by a thin layer of such a properly waterproofed material between the inner and the outer sole, since no leather is really and permanently impervious to water when subjected to the kneading action of the foot. Passing from the use of such materials as splits to that of the really solid leathers used for outer soles, we find great differences in their wear and impermeability. Some tannages naturally give soft and porous as well as light weighing leather, while others produce it heavy and solid, and the soft and porous leathers are unsuitable for our wet climate, though, perhaps, even better than the harder ones for drier countries or for indoor use. It cannot be too often repeated that the shoe manufacturer is blind to his own interests and to those of his customers in his excessive insistence on color and finish in English sole leathers, while he neglects both of these points in American leather, and thus drives much good money across the Atlantic which would come round again to him sooner if it were kept on this side. The demand for light colored leather (which is afterwards blacked or faked on the sole) limits the tanner excessively in the choice of his tanning materials, and excludes several which are excellent—as regards solid wear, while the extra finish as compared to American sides increases cost at least ½d. per pound. It also tends to the use of bleaching processes, which improve color at some cost, but to the detriment of wear and water resistance.

The temptation to add weight to sole leather naturally arises from its sale by weight, but it is difficult to find any other standard so convenient and so applicable, and its effect has been modified of late years by the improved costing methods of shoe manufacturers, which make bulk or thickness a consideration almost as important. It must not be forgotten that the most costly constituent of leather is the hide, which calculated to dry material costs the tanner, say, 1s. 8d. per pound, while the dry material of tanning extracts may be bought for, say, 3d. Normal leather contains roughly equal parts of these constituents, and the commercial success of the sole leather tanner largely depends on his skill on increasing the proportion of the cheaper ingredient, and

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in making the largest possible quantity of leather from the least quantity of hide. This has to a certain point its advantage, since fully tanned leather is much less permeable to water, and undertanned sole leather is almost a thing of the past; but without claiming that leather is a definite compound of hide and tannin, it is found impossible to make the hide really combine with more than about its own weight of tanning substances; and any extra quantities of tanning extract which it contains are for practical purposes as much of an adulterant as the same weight of glucose and dextrine, since they can be washed out in the same way. The addition of some, and even considerable, excess of tanning matters is unavoidable in practice, since it is only in presence of excess that the hide will really combine with the maximum quantity; and very strong solutions are also essential to quick tannage, but when, as is the case with many English sole leathers, the amount which can be washed out with cold water reaches 30 per cent. of the whole, it is clear that things have gone too far, and that from the users' point of view the addition of a few per cent. of glucose and magnesium chloride is a comparatively venial offense. I have analyzed many foreign and colonial leathers which I have been obliged to report adulterated, which yet contained less total of water-soluble matter than many unadulterated English tannages. I would strongly draw the attention of manufacturers to the question of loss on washing, not merely as regards loss of weight, but of firmness and apparent quality Much of the firmness of the cheaper leathers is due, not to solid tannage, but to the quantities of dried-up extract which they contain. A simple way of testing the matter is to take two pieces of similar leather of equal weight, say two cut soles, and to wash one by thorough soaking in cold or tepid water with frequent squeezing and kneading, and then to dry the two pieces side by side under the same conditions, when loss of weight of the washed piece will be at once apparent.

With regard to the weighing of upper leathers I need say little, since when sold by the foot or dozen any weighting for weight's sake would be futile. Curried leathers of the heavier classes still sold by weight, and especially strap butts, are still often heavily loaded with glucose, with or without barium chloride, magnesium sulphate, and other salts, and I fear a few kips are still weighted with barytes drummed in with the grease. It is significant that

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the amount of barytes profitably mixed is enormously in excess of the legitimate uses of baryta salts, but the surplus does not all go into leather. These forms of loading are absolutely indispensable, and I should be glad to see them made here a criminal offense, as they are in Germany. There is, however, another form of loading, with large quantities of hard greases, which stands in much the same category as the weighting of sole leather with superfluous tan. Originally practised on American glove grain, waxed calf and waxed splits, it is now largely practised in Europe, though hardly so much as in the country of its origin. Up to a certain point the grease is advantageous, and increases the wear and waterproofness of the leather, but when the greases reach 45 per cent. of the total weight, as in some American leathers, they may fairly be regarded as excessive. It is noteworthy that this form of loading largely obtains in goods which are nominally sold by measure, but into which the question of weight enters by the fact that they are specified to weigh so many ounces to the square foot. Of course, the grease, being light, increases the bulk and apparent substance, enabling a thinner hide or split to be used.

In the lighter and finer leathers used for foot covering adulteration properly so-called can hardly be said to exist, inferior quality being generally due either to the character of the original skins or to the want of knowledge and skill of the tanner. Very injurious substances such as nitric acid are often used in the finishing of the cheaper colored leathers, and lead is largely employed in bleaching. On the other hand, the objection justly raised to the use of East Indian and other catechol tannages for bookbinding and upholstery hardly applies for foot covering, since the leathers are sound and durable as regards mechanical wear, and will probably be worn out and thrown away long before the decay of time can set in. The presence of grease or oil in any leathers which must be brought in contact with patent leather, while it cannot be classed as adulteration, is a serious and destructive defect.

The adulteration of textile linings has often proved also a serious matter for the manufacturer, for the consequences of which he is apt to blame the innocent tanner. I have scarcely examined a sample of lining which was free from magnesium and sodium sulphates, and swansdowns especially are often loaded with 30, and in one case with nearly 50 per cent. When such a lining is worn on hot and damp feet the salts absorb the moisture and the

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lining remains permanently damp and unwholesome, and the salts crystallize through the leather and entirely spoil its outside appearance. The cost of a respectable lining is so comparatively small that it seems to the outsider something like the proverbial 'spoiling the ship for a ha'porth of tar." I have not yet found a case where the damage arose from salts in the leather. Fat, however, sometimes "sprouts" from badly manufactured box calf and glacé kid, and still more frequently from calf kid, with much the same appearance, but it is easily removed by warming, or by rubbing with petrol or benzine. A resinous exudation (spueing), which sometimes occurs on heavily stuffed leathers, is best treated with a mixture of benzole and methylated spirit.

## REVIEWS

**The Direct Estimation of Hide-Substance Dissolved in Lime and Tan-Liquors.** R. A. EARP. *Collegium*, 1907, 285, 412.—The author gives the following method of separating the colloidal nitrogenous matter in the liquors which gives a trustworthy determination of the loss of hide-substance incurred through solution in the liquors and is based on rendering insoluble the dissolved colloidal hide-substance with another insoluble colloid, separating it from the liquor and determining the nitrogen. One hundred cc. of the settled, or roughly-filtered liquor are treated with 10 cc. of a 10 per cent. solution of acetic acid, and 10 cc. of a 10 per cent. solution of lead acetate. The mixture is allowed to stand for half an hour with an occasional shake. A plug of cotton-wool is inserted at the bottom of a funnel whose neck has been broken off. The mixture is then filtered through the cotton-wool, a few drops being added carefully at first to make the cotton-wool settle down. When the cotton-wool is properly wetted the funnel may be filled with the mixture. The filtrate should be quite clear and colorless. When all the mixture has been added, and the funnel is about half full of the flocculent precipitate, it is filled up with water, allowed to filter through till half full, and filled up again with water. This is repeated several times, care being taken that the funnel never gets less than half full of liquid, otherwise the precipitate gets into a compact mass which is difficult to wash. The funnel is then removed to a tall glass vessel filled with water, into which it fits, about two-thirds of the height of the funnel being within the vessel. Here the funnel remains for two days, being filled at intervals with water, and the water in the vessel also being changed. The precipitate is occasionally stirred up if it is inclined to solidify too much. In two days time the precipitate may be considered to be completely washed, for all the time the funnel is in the vessel, it is being washed by diffusion and convection into the large volume of water below it. The precipitate is then drained, and tested for nitrogen. For weak tan-liquors lead acetate is the most convenient reagent to use and for lime-liquors chrome alum is the best.

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**On the New Tannin Guarantee.** E. MUELLER. *Der Ledermarkt*, 1907, 90, 13.—Mr. Erich Mueller, President of the Association of German Color and Tanning Extract Manufacturers, in replying to the article of Mr. F. Roser says that the circular issued by the Association was not a criticism of the new method but a statement saying that the old method would be retained. The author states the aim of the Association has been to have concordance in results of analyses, especially between the different laboratories and that a new method must show this concordance. This has still to be proven of the new method. The internationality and the interests of the foreign countries, the author says, won in working out the new method. The author states that Mr. Roser agrees that with extracts made from the same raw material but made in different factories the differences between the two methods vary. The author wishes to add, from practical experience in the extract industry, that these differences vary even with the same kind of extract made in the same factory, the reason for this no one being able to give. Consequently the extract manufacturers, on account of this uncertainty, cannot give a binding guarantee by the new method. Furthermore, the remarks of Mr. Roser are all based on the statement that the new method determines the amount of tannin more accurately, but this has never been proven. The author also states that in the filter method more substances of the extract combine with the hide than in the shake method and does not see the reason why these substances should not be tanning matter. It is more natural to believe that the shake method does not absorb all the tanning matter. As regards the statement of Mr. Roser that the German extract manufacturers sell their extracts to foreign countries guaranteed on the new method, the author says that such a case is not known to them.

**Comparison of Filter Method with Official (M. and S.) Powder, with Shake Method with Various Powders.** H. R. PROCTER. *Collegium*, 1907, 286, 423.—In a letter to Professor Dr. H. Becker, Professor Procter encloses the results of a number of analyses carried out both by the filter and shake methods, showing the relative percentages obtained and the differences in each case between the two duplicates. The official Freiberg powder was used in these tests which was very poor, containing much more than the authorized amount of soluble hide-substance. The author is of the opinion that much better results would have been obtained with Dr. Paessler's lightly chromed powder, but this powder has never been officially sanctioned. The results showed that in many cases the shake method gave higher tannin than the filter method, and in oakwood extract the results by the filter method showed extreme steadiness in the extract while those of the shake method indicated considerable differences. The author is of the opinion that these are due to the differences in the manufacture of the extract, the same not being shown by the filter method. Thus the extract manufacturers obtain valuable information by the shake method when applied to works control.

**Bleach for Red Leather.** *Shoe and Leather Reporter*. December 5, 1907, p. 21.—It is stated that a hot solution of wood alcohol applied with a camel's hair brush to red union leather, after buffing, will produce a fine white bottom for taking any light stain. The alcohol should be heated, very hot, over steam or hot water.

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**On the New Tannin Analysis.** F. ROSER. *Der Ledermarkt*, **1907**, 90, 13.—The author states that the Association of German Color and Tanning Extract Manufacturers published an article in which they severely criticized the new international method of tannin analysis, to which as a tanner he wishes to reply. The extract manufacturers quote as the greatest fault in the new method that at present it is not possible to say that the new method gives so and so much lower tannin than the old method. This the author states is not an error but is the strongest point in the new method, for if there were a definite difference between the two methods it would not have been necessary to make the change. The results between the two methods show with different extracts in some cases large and in some cases small differences, also with the same kind of extract made by different firms this being the case. From this the author states the tanners can draw valuable conclusions in judging extracts of different manufacturers. All tannins and extracts contain variable amounts of non-tannins, which according to the old method are determined as tannin, while with the new method the same are determined as non-tannins. Therefore, it stands to reason that the more non-tannins an extract contains the greater will be the difference between the old and new method and the lower will be the tannin found by the new method. It is apparent that the old method offers greater advantages for a poor product than the new method. The extract manufacturers speak in their article of differences in the methods up to 8.8 per cent. This large difference was found with one extract out of 80 analyses made in Freiberg. In all the analyses made in the author's laboratory on various tanning materials the highest difference was 2.8 per cent. in one extract. Similar differences between the two methods were also found in other laboratories. In case such a large difference should happen with a poor product, then this could not be considered a fault of the new method which gives in itself such surprisingly close duplicates. The extract manufacturers claim that there is uncertainty in the determination of the insolubles, but surely this can not be held against the new method as the specifications for this determination have not been changed. In closing, the author states that he is informed from letters from his foreign friends that all the tannin analyses are made by the new method to the greatest satisfaction of the tanners and extract manufacturers. Only in Germany the introduction of the new method has been retarded by the opposition of the German Extract Manufacturers, but the author hopes that in future the German tanners will insist on a guarantee by the new method and that the extract manufacturers will not force the German tanners temporarily to buy their extracts in foreign countries, where they will receive a guarantee by the new method. An interesting fact is that the German extract manufacturers sell their extracts to foreign countries under guarantee by the new method.

**On the Question whether an Amount of Sulphuric Acid Influences the Quality of Leather.** W. EITNER. *Der Gerber*, **1907**, 794, 795, 796, 797, 267, 231, 296, 309.—The author gives an account of experiments carried out in order to determine the effect of sulphuric acid in leather and states that from practical experience leathers which had been kept at the experiment station for many years and which contained small amounts of sulphuric

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acid remained in good condition. Experiments were carried out in which differently tanned leathers were treated with different amounts of sulphuric acid, the action on the same noted and the amounts contained in the same determined. Furthermore, the tensile strength, the stretching, the kind of break and the degree of resistance of the grain determined. The results showed a decrease in the ash of the leathers treated with sulphuric acid, which is accounted for by the formation of acid salts which are more soluble than the neutral or basic salts and which are removed on washing. Although increasing amounts of sulphuric acid were put in the leather the amounts of free sulphuric acid found in the same were about equal. From this the conclusion can be drawn that only a certain amount of the sulphuric acid put in the leather is held back by the same, the balance being washed out. The results also showed after storing from fourteen days to five months that the tensile strength of the leather is not impaired, but on the whole slightly improved. The coefficient of stretching showed wide variations, but this is accounted for because the different parts of the skin are very irregular. All in all, the stretching property was increased which also showed that the leather was not damaged. The author found that sulphuric acid is bound by organic substances as well as inorganic substances in leather and that where free sulphuric acid is present the character of the leather is changed and impaired, this being due to larger amounts which are practically never met with. Tanned leathers affected by sulphuric acid are less stiff and hard than they would normally be, and break without a cracking noise. Similar to this are leathers which have rotted by damp storing and are hard to distinguish from the former. Leathers heavily loaded with extracts, glucose and salts, are also brittle but act different than the others as they break with a cracking noise and are more difficult to tear. The author recently tested such a sample of leather which contained no trace of free sulphuric acid but 25 per cent. of substances not combined with the hide-fibre which consisted of 5 per cent. of barium chloride, 4 per cent. of glucose and 16 per cent. of uncombined extract. After washing out these substances the leather was no longer cracky but normal and could not be torn. A leather attacked by free sulphuric acid could not be restored, but remained valueless; consequently, through washing, leather which has been damaged by overloading can be distinguished from leather damaged by free sulphuric acid. Some experiments were carried out by the author with oxalic acid which gave results similar to those of sulphuric acid. The author states that sulphuric acid has only been classified as combined with mineral matter, which is considered harmless, and sulphuric acid which appeared not to be bound to mineral matter and considered free and therefore harmful. The tests of the author showed that not only is sulphuric acid combined with mineral matter but also can be bound in considerable amounts to the organic substance of the leather, and which the tests showed is also harmless. The amounts of organic combined sulphuric acid vary with the different kinds of leather, but as a maximum 1.3 per cent. can be accepted. The author considers 1 per cent. sulphuric acid to be a proper amount allowable for all leathers. This amount would be composed of about 0.2 per cent. coming from the sulphur of the hide, about 0.2 per cent. when

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a sodium sulphide lime was used and 0.4 per cent. from the plumping with sulphuric acid, so that only 0.2 per cent. would remain for acid gotten into the leather later.

**The New International Tannin Analysis and Short Communications on Tanning Extracts.** F. ROSER. *Collegium*, **1907**, 283, 284, 397, 402.—The author gives an account of the old and the new method of tanning analysis with the object of explaining to the German tanners the reasons for adopting the new method and the benefits of the same. In speaking of tanning extracts the author states that sulphited extracts easily penetrate into the skin and give the leather a light color, but the same do not combine with the hide as well as sulphite-free extracts and can be washed more readily out of the leather. It is evident that the sulphited extracts give less gain than other extracts in tanning. The insolubles in ordinary quebracho extract, when the extract is used in the latter part of the tannage, increase the gain and give strength and compactness to the leather. Experiments carried out in an English laboratory in order to compare the water penetration of old and modern sole leather resulted when using a metal cylinder of about 30 to 40 cm. high and fastening the leather on the bottom and filling the cylinder with water, that the water penetrated the leather tanned according to the old methods, in seven days; the leather tanned by the modern methods in four to five months by using extract, in three to four days; and the leather tanned in the wheel, in a few minutes.

**The Tanning Extract Manufacturers and the New Method of Tanning Analysis.** W. EITNER. *Der Gerber*, **1907**, 793, 323.—The author speaks of the new method of tannin analysis and the circular published by the Association of German Color and Tanning Extract Manufacturers regarding the same. The circular shows that the German quebracho extract manufacturers are not satisfied with the new method because the same gives lower and more correct results and is not so suitable for the adulteration of the extracts. But these extracts are made for the tanner for whom the adulteration means a great deal, as the resulting leather is dependent on the knowledge of the material used. The reduction in the tannin is more pronounced with the quebracho extracts now found in commerce, so that this shows the reason for the opposition of the extract manufacturers. The extract manufacturers try to prove that owing to the differences in the results between the two methods varying a great deal, the old method always gives more correct results, on account of constancy, than the new method which gives variable results. The author says it is sad as well as ludicrous that the consumer, the tanner, who is the most interested party, should not be considered in this controversy. Furthermore, it is a deplorable fact that an institution erected for the benefit of the tanner, helps their adversaries as is the case. On the part of the tanner it would be lamentable if it remains thus, and that the extract manufacturer can dictate to him the clauses in the contract, the method of analysis, and the guarantee laboratory. It is hard to conceive how able business men, as the German quebracho extract manufacturers are, would take such steps as they have without other support, and they could do this only when they were sure of the support of control laboratories.

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**Tanning Materials and Manufacture of Leather in Jamaica.** M. NIERENSTEIN. *Collegium*, 1907, 286, 420.—The tanning materials used are divi-divi and red and white mangrove bark. Bastard logwood is also found and the author is of the opinion, owing to the relation between divi-divi and algorabilla with the logwood, that the bastard logwood might be used as a tanning material. The bastard logwood does not contain the dye-stuff and A. G. Perkin and also the author have found that there is a close relationship between the tannins and coloring matters in the plants and that as the amount of coloring matters decrease the tannins increase. The cultivation of the white mangrove should be very successful as this material could be used for tanning light leathers. Apparently there is very little breeding of cattle, sheep, etc., in the island, although plenty of good pasture land is available. The leather industry is still undeveloped, there being only twenty-one tanneries, employing in all fifty-five persons and producing yearly from twenty-eight to thirty-one tons of leather. The importations of raw and manufactured leather are large, and the author is thus of the opinion that the leather industries of Jamaica might be developed and suggest the following methods: (1) To develop the cultivation of tanning trees and plants, especially the white mangrove. (2) To investigate the question of the bastard logwood in respect to tanning properties. (3) To introduce tannin containing plants from the other West Indian islands, and the Quebracho Colorado. (4) To encourage the breeding of cattle and sheep, and to try to introduce the Barbados sheep. (5) To develop tannin extract works, it would be advisable to try with primitive methods, similar to those used in South America, and to develop them afterwards into more modern methods. (6) To develop the present important industry of leather manufacture.

**Answer to R. A. Earp's Article on the Influence of Small Amounts of a Chrome Salt on the Tannin-Gelatine Reactions.** E. STIASNY. *Der Gerber*, 1907, 798, 326.—The deductions of Earp from the non-precipitation of chrome salts with tannin and with gelatine the author does not consider conclusive. Earp says that acid solutions of chrome salts do not help precipitation but can act only in the opposite way as they themselves do not give precipitates with the two stated components. The author states that he has shown with metaphosphoric acid and oakwood non-tannins, which also do not give precipitates with various tannins or with gelatine, that nevertheless an increase in the delicacy of the tannin-gelatine reaction takes place. The manner in which Earp carries out the reaction was shown by Procter (*Collegium*, 1907, 262, 223) to be unsuitable. Procter pointed out that by adding hydrochloric acid to a solution of gelatine-salt a precipitate can be obtained with definite concentrations. Reed (JOURNAL OF THE AMERICAN LEATHER CHEMISTS ASSOCIATION, II, 160) tested the reaction according to Earp and obtained results which do not substantiate Earp's statements but fully agree with the ones of the author. The author states that the agreement of the results of Procter, Reed and his own are sufficient to discredit the statements of Earp.

**The Acidity of Tan-Yard Liquors.** H. G. BENNETT AND C. D. WILKINSON. *J. S. C. I.*, No. 22, Vol. XXVI, 11/30/'07, 1186–1188.—The authors present a series of experiments, with various methods, on artificial liquors of pre-

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cisely known composition. Owing to the very unsatisfactory nature of the "charcoal method," it is not taken into consideration, but special attention is called to the "lime water" method of Procter, which, as stated, has scarcely received full justice. In titrating a solution of pure gallotannic acid the lime water gives plus results but this is not regarded as a blank experiment, or as the true extent of error in the end-point on similar acidified solutions since the ionic equilibrium in the latter case is of totally different order. In the following experiments all solutions were made to contain 0.4 per cent. of dry tannin regardless of the acidity variation.

| Liquor. | cc. lime water required by 10 cc. liquor. | cc. lime water required by 10 cc. N/10 hydrochloric acid. | cc. N/10 potass. hydrox. for 100 cc. liquor. |
|---|---|---|---|
| N/20 acetic acid | 11.65 | 22.2 | 52.1 |
| N/40 acetic acid | 6.5 | 22.3 | 29.1 |
| N/20 formic acid | 10.45 | 22.2 | 47.0 |
| N/40 formic acid | 5.7 | 22.2 | 25.6 |
| N/20 lactic acid | 10.8 | 22.9 | 47.1 |
| N/40 lactic acid | 5.8 | 22.9 | 25.8 |
| Theoretically N/20 acid should give | | | 50.0 |
| Theoretically N/40 acid should give | | | 25.0 |

Although the results are not correct theoretically, "The figures obtained are always an accurate indication of the amount of those acids which are capable of forming soluble salts with lime." The authors state that the "quinine method" does not show any material increase in accuracy, even with gallotannic acid. Unless allowed to stand for some time, the mixtures of quinine and tannin infusion filter badly, and after standing darken perceptibly. Objection is made to the large amount of indicator necessary, and to the rapid fading of the end-point. The apparent cause of these difficulties is the presence of hydroxy compounds which do not form insoluble quinine compounds. The method is also inapplicable in the presence of boric acid.

| Liquor used, all 0.4 per cent. tannin. | cc. N/10 potass. hydrox. for 100 cc. liquor. | Do. corrected for possible influence of acidity in the tannin. |
|---|---|---|
| No added acid | 3.3 | .. |
| N/20 acetic | 51.7 | 48.4 |
| | 52.8 | 49.5 |
| N/40 acetic | 27.5 | 24.2 |
| N/20 formic | 42.9 | 39.6 |
| | 48.4 | 45.1 |
| N/40 formic | 23.1 | 19.8 |
| N/20 lactic | 49.5 | 46.2 |
| N/20 boric | 13.2 | 9.9 |
| | 15.4 | 12.1 |
| N/20 gallic | 71.5 | 68.2 |
| | 63.8 | 60.5 |

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Experiments with the "gelatine precipitation method" indicate the absorption of acid by the gelatine, when the latter is present in sufficient quantity to remove nearly all the tannin. When not present in sufficient quantity, the end-point is indefinite, and too much acid appears to be estimated.

| cc. of liquor used. | cc. of gelatine solution used. | cc. of water added. | cc. of N/10 potass. hydrox. for 100 cc. liquor. |
|---|---|---|---|
| 25 | 5 | 20 | 49.2–51.6 |
| 25 | 10 | 15 | 49.2–50.8 |
| 25 | 15 | 10 | 49.2–50.0 |
| 25 | 20 | 5 | 49.2–49.6 |
| 25 | 25 | .. | 48.4 |
| 25 | 30 | .. | 47.6 |
| 25 | 35 | .. | 46.8 |
| 25 | 40 | .. | 46.5 |
| 25 | 45 | .. | 46.3[1] |
| 25 | 50 | .. | 46.2[1] |

The magnesia method is open to the objections that it is laborious in the presence of other bases; is capable of forming basic salts in the presence of acetic and formic acids; yields dark filtrates in presence of gallic acid; all magnesium tannates are not insoluble; and magnesium may be present in the tan liquors. The authors are inclined to think that in lead oxide is the possible solution of the acidity question. By its use all tannins are precipitated, and sulphuric, oxalic, boric and carbonic acids removed, leaving the lead salts of acetic, formic and lactic acids in the clear filtrate. Both the lead and the combined organic acids can be quickly determined volumetrically, and the authors hope soon to be able to publish the results of their investigations along this line. Experiments are also in progress, upon a hide-powder method, using the basic chloride shake method, and after agitation, titrating the free acids without the removal of the hide-powder. Results of this method will be published shortly.

**The Volumetric Determination of Chromium by Potassium Permanganate.** H. BOLLENBACH. *Collegium*, **1907**, 287, 428.—The author states that he observed some time ago that potassium permanganate is decolorized by chromous salts. When a halogen-free solution of chrome alum is boiled with a solution of potassium permanganate, the color of the permanganate disappears in a short time and on further additions of potassium permanganate continues to do so until all the chrome salt has gone over into chromate. The green color of the chrome solution gradually goes over into the yellow or yellow-red of the chromates. The reaction takes place according to the following equations: $6KMnO_4 + 5Cr_2(SO_4)_3 + 3H_2SO_4 + 16H_2O = 10H_2CrO_4 + 6MnSO_4 + 3K_2SO_4 + 9H_2SO_4$ or $3MnO_4' + 5Cr''' + 4H^{\cdot} + 8H_4O = 5CrO_4'' + 3Mn'' + 20H^{\cdot}$. This reaction takes some time and the change from the red bichromate color to the violet permanganate color is hard to detect, owing to a mixed color being produced. Considerably faster and with more accuracy the end is arrived at if the determination is carried out similar to Volhard's titration of manganese in which the potassium per-

[1] Tannin just detectable in filtrate.

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manganate is reduced only to manganese peroxide. The author states that he observed in a hot solution containing very little nitric acid in presence of 10–15 grams of potassium nitrate the reaction is very rapid, almost instantaneous, and gives a splendid color change if the produced chromate is precipitated by lead nitrate which is added before beginning the titration. The equations

$$2KMnO_4 + Cr_2(SO_4)_3 + 4H_2O = 2H_2CrO_4 + K_2SO_4 + 2MnO_2 + 2H_2SO_4$$
$$MnO_4' + Cr''' + 4OH' = MnO_2 + CrO_4'' + 2H_2O$$

show that for the oxidation of one $Cr'''$ one $MnO_4'$ is necessary, so that the limits of error are five times more favorable than in the titration of iron by potassium permanganate. Whereas, 1 cc. of N/10 $KMnO_4$ solution is equal to 5.6 mg. of iron, 5.2 mg. of chrome are indicated by 5 cc. of the same potassium permanganate solution. The titration is carried out by placing in a flask of 400–500 cc. capacity 10–15 grams of potassium nitrate, 2–5 grams of pure lead nitrate, 4–5 grams of barium sulphate and then about 100 cc. of hot distilled water. Potassium permanganate is then slowly dropped in from a burette until the violet color becomes permanent. For this, 2–6 drops of potassium permanganate solution, according to the purity of the reagents, are necessary, which must be deducted in the titration. The chrome solution is then added and diluted to about 400 cc. The solution must contain only a little nitric acid and no halogens or other reducing substances. In case the chromous salt is present as sulphate the presence of lead produces a precipitate of lead sulphate which helps, similar to the added barium sulphate, to settle the precipitate produced on titration. The mixture is heated to boiling, the potassium permanganate solution added and shaken well. The violet color soon disappears and the formed precipitate of manganese peroxide and lead chromate rapidly settles. The solution above the precipitate remains greenish or nearly colorless as long as chromous ions are present, and only after complete oxidation is the handsome permanganate color obtained, which should not disappear on standing from fifteen to thirty minutes on the water-bath. The temperature in the flask must be kept at 90–100° during the whole titration. The addition of barium sulphate especially hinders the peroxide from precipitating on the walls of the flask which would stop the transparency and make the end reaction hard to see. The author states that the first red coloration should not be taken as the end-point of the titration, but the plainly visible violet color, as 2–3 drops of permanganate solution in excess would make the result in most cases only a very little higher.

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## PATENTS

**Substance for Treating Hides and Process of Making Same: U. S. Patent No. 873,074** to O. H. NOWAK, Chicago, Ill. This patent covers the manufacture and use of the trade article known as Dermiforma. The curd of milk is precipitated by heating the milk and adding sour liquor obtained from previous treatment of milk. The curd is removed and the whey is

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allowed to ferment until 1 per cent. acidity (calculated as lactic acid) develops; the fermented whey is then concentrated *in vacuo*.

**Process of Manufacturing Artificial Leather: U. S. Patent No. 873,582** to L. GEVAERT, Naert, Audenarde, Belgium.—Consists in dissolving an albuminoid substance in a suitable solvent, adding a tanning agent thereto; dissolving the tanned albuminoid, and impregnating *in vacuo* felted tissues with this latter solution, and finally evaporating the solvent so that the tanned albuminoid remains on the dried fibers of the teazeled or felted tissues.

**Process of Carroting Hides and Skins: U. S. Patent No. 873,594** to C. and E. PICHARD, Paris, France.—A process of carroting which consists in subjecting the hides to the action of a jet of carroting liquid sprayed under pressure of steam while fed in the direction of an acute angle to the hides, so that the hairs are raised and their roots exposed by the action of the spray of carroting liquid

**Manufacture of Tanning Extracts with Waste Sulphite Cellulose Dyes:** D. STEWART. **English Patent No. 5,438.**—The author describes a process of leaching tanning materials with the clear filtered sulphite liquors. The liquor is drawn off into settling tanks, and the clear supernatant liquor evaporated in the usual manner. The bleaching effect of the sulphites may be increased by using oxalic or other suitable acid.

**Apparatus for Tanning Skins.** P. PANO and A. BOGLIO. **French Patent No. 378,613**—The skins are suspended in a series of connected vats through which the liquor circulates from one end to the other. An outside trough is provided so that any vat may be cut out without interfering with the system. From a cistern at the end of the series, the liquor is pumped into a receiving tank placed at a higher level at the beginning.

**Manufacture of Varnished and Multi-Colored Leather.** GEBR. FELDMANN and H. FELDMANN. **French Patent No. 378,643.**—The leather is covered with an opaque color, consisting of a coloring matter mixed with lacquer, and then dried. A second coating is given, and while still moist, the leather is rubbed smooth, after which the process of drying and coloring may be repeated if necessary.

**Machine for Cutting Leather, Etc., into Continuous Strips: U. S. Patent No. 874,102** to F W. MERRICK, Boston, Mass.

**Leather Working Machine: U. S. Patent No. 873,790** to J. ROOD, DANVERS and F. J. PERKINS, Woburn, Mass.

**Depilation and Soaking Process for Skins.** J. MOREL and P. SAVIGNY. **French Patent No. 378,425.**—Skins are soaked in a solution of sulphuretted compounds of antimony, such as sulphoantimonates and sulphoantimonites of the sulphides of the alkalis and alkaline earths. The strength of the solution, and the time of contact depend upon the nature of the skins.

**Artificial Leather and Process of Manufacture of Same.** J. P. GANTHIER. **French Patent No. 379,094.**—Eight parts of any kind of fiber are amalgamated with two parts of caoutchouc. The materials can then be formed into sheets or pressed into any desired form, vulcanizing if required.

**Process of Stuffing Leather and Apparatus Therefor: U. S. Patent No.**

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**874,882** to G. BEARHOPE, Columbus, Ind.—The hides are placed on a perforated topped table, and the stuffing mixture is applied through a spray nozzle on a hose leading from a tank containing the stuffing mixture under pressure. The apparatus covered by the patent consists of a melting tank, a compression storage tank, means whereby pressure is generated within this tank, a spray nozzled hose connected to the storage tank, and a perforated topped table provided with means to collect the excess of stuffing mixture.

**Process of Bating Hides and Skins: U. S. Patent No. 875,382** to O. ROHM, Stuttgart, Germany.—A process of bating consisting in subjecting the hides and skins to the action of an aqueous solution of sulphureted hydrogen, carbonic acid, and ammonia.

**Device for Cutting Bark from Trees: U. S. Patent No. 875,391** to W. T. TINSLEY, Custer, S. D.—An improved spud, or bark-peeling instrument.

**Feed-Roll for Leather Skiving Machines: U. S. Patent No. 875,528** to A. HIRTH, Caunstatt, Germany.—An inner convex feed-roll made up of a number of individual rollers of different diameters, which works in connection with an outer concave feed-roll also subdivided into a number of individual rollers of different diameters.

**Liquid Leather Dressing: U. S. Patent No. 875,653** to G. W. CHILDS, New York.—A leather dressing adapted for impregnating leather, derived from sapped organic tanning liquors.

## BOOKS RECEIVED

MERCK'S 1907 INDEX (third edition). An encyclopedia for the chemist, pharmacist and physician, stating the names and synonyms, source of origin, chemical nature and formulae, physical form, appearance and properties, melting- and boiling-points, solubilities, specific gravities, methods of testing, etc., of the chemicals and drugs used in chemistry, medicines and the arts. 472 pages, cloth. New York: Merck & Co. Gratuitous to users of chemicals upon receipt of 25 cents to cover expenses incidental to delivery.

The general scope and character of this book are made sufficiently plain in the sub-title; it is a chemical encyclopedia on the order of Beilstein, treating only those chemicals and drugs actually on the market. This latest edition of this work has been improved by the addition of information concerning the newest products, by the adoption of the latest nomenclature, by the adherence to the most modern authorities, and in many cases by the verification of data. Comparative values of the chemicals are given by a system of numbers, so that the relative values may be easily found.

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CHEMICAL REAGENTS, THEIR PURITY AND TESTS. By E. MERCK; authorized translation by H. SCHENCK. New York: D. Van Nostrand Company. 1907. 8vo. cloth, 241 pp. $1.50 net.

A new and improved text based on and replacing the latest edition of Dr. C. Krauch's, "Die Prüfung der Chemischen Reagentien auf Reinheit," which has been the standard work of this character.

The translator presents the translation with several changes and additions to adapt the work to American needs, and in the hope that until the work of the Committee on Purity of Reagents, appointed by the American Chemical Society in 1902, is published, this translation of Dr. Krauch's well-known work will be generally accepted as a standard for specifications of purity of reagents.

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## ELECTIONS

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## ACIDITY OF HIDE-POWDER

*By F. H. Small*

The writer's attention has been called to a paper appearing in the February issue of the JOURNAL by H. Garner Bennett, M.Sc., in which Mr. Bennett takes occasion to criticize the report of last year's committee of the A. L. C. A., which did some work on the relation between the acidity of the hide-powder used in making a tannin analysis and the non-tannin value obtained. Mr. Bennett's criticisms relate first to the method suggested for determining the acidity of the hide-powder and second to the results obtained by the use of hide-powder of different acidities.

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On the first count, Mr. Bennett argues that the committee were not justified in rejecting[1] the method proposed by him[2] for determining the acidity of hide-powder on the evidence obtained, inasmuch as they failed to carry out the method as prescribed—they assuming the titration to be complete before such was the case. Mr. Bennett is probably correct—the error of the committee being due to a wrong assumption as to the meaning of the word "permanent." It was assumed that a pink lasting fifteen minutes was "permanent" in the usual parlance of chemistry—an assumption that later work has shown was not warranted. The neutralizing process goes on so slowly as the end-point is neared that it is necessary to give the word "permanent" more nearly its dictionary meaning and understand by it a matter of hours rather than minutes. When carefully carried out with this interpretation and with precaution to eliminate the action of the carbon dioxide of the air, it is possible to secure concordant and accurate results if the alkali be added in sufficiently small quantities and the patience of the operator be not exhausted. A day's time is usually required, and as stated in the report of the committee the titration is tedious.

Mr. Bennett next criticizes as follows the alternative indirect method urged by the committee—"if the principle of this *modification of the author's method* were correct, surely it should be possible to obtain equally concordant results and a greater accuracy by using a small excess of alkali." The italics are the writer's.

The indirect method is hardly a modification of Mr. Bennett's method as he so calmly claims, for, as stated in a report of the committee, the idea of this method was suggested to the chairman in a letter by Mr. Teas and a method founded on this idea had been in use in Mr. Teas' laboratory since 1903 for determining the acidity of hide-powder.

The point, however, which Mr. Bennett makes regarding the undesirability of the addition of so large an excess of alkali as suggested in the report of the committee, is well taken. At the time of writing the report the experiments of the chairman had pointed to the conclusion stated, that the results were independent of the amount of added alkali, and consequently he felt safe in advocating the use of an amount of alkali sufficient to

[1] Journal A. L. C. A., II, p. 348.

[2] J. S. C. I., 1907, p. 455.

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neutralize the acid in any usable hide-powder. Further and more extensive experiments, however, have since shown that the use of a large excess of alkali is undesirable. These later experiments, while showing that the chairman was not wise in his prescription of details, have likewise shown that the indirect method of titration is much more expeditious than the direct and susceptible of equal accuracy.

The writer would hardly care to estimate its accuracy by the procedure suggested by Mr. Bennett using a hide-powder delimed with hydrochloric acid, then neutralized with sodium carbonate, dried, ashed, etc., as this procedure differentiates in no wise the chlorine that may be present in the hide-powder in combination as chloride from that in combination as acid. The fact, however, that the indirect method when used with the necessary precautions gives the same result as the direct when also used with the necessary precautions would seem to indicate that both methods are giving correct results.

The procedure used by the writer in these later experiments and which he has found to work satisfactorily is as follows: To 5 grams air-dry hide-powder in a stoppered flask, add 75 cc. water and a measured amount of N/10 alkali which is from 3 to 5 cc. in excess of that required to neutralize the acidity of the hide-powder. (This may be determined by a rough preliminary test if not already known.) Digest for 60 minutes, add 1 cc. of phenolphthalein and titrate back the excess of alkali with N/10 acid, adding the acid cautiously as the end-point is neared and shaking vigorously after each addition.

The writer feels confident that if Mr. Bennett will take the trouble to compare on the same hide-powder his direct method and the indirect method as outlined above, Mr. Bennett must agree that either will yield a correct result and that the indirect is much less trouble and gives results in a much shorter time.

In the final choice of a method the writer must confess that he sees no real call for an appeal to sentiment; that method which excels in speed and accuracy should be given the preference and he is perfectly willing to accept as standard the method which in the judgment of his colleagues best fulfils these requirements.

On the second count of Mr. Bennett's indictment there is little to be said. Mr. Bennett falls back on the comfortable assertion

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that he has "still no doubt that a higher acidity involves a higher absorption of non-tannins by hide-powder and hence a more incorrect result." This may be satisfying to Mr. Bennett, but it fails to explain why the contrary was found by *all* the members of the A. L. C. A. Committee of last year, a concordance in the committee which practically eliminates the personal factor as the cause of the difference. The only conclusion that seems to the writer deducible from the results so far obtained is that we still have much to learn.

## THE NATURAL DYESTUFFS STILL USED IN LEATHER MANUFACTURE[1]

*By J. W. Lamb*

### *Logwood*

Logwood is, perhaps, the only natural dyewood that the leather dyer cannot really do without, and will be used in conjunction with salts of iron for the production of blacks upon leather for some years to come. It is grown in Jamaica, St. Domingo and Honduras. There are several kinds of the logwood-producing tree, differing in both the color of the wood itself and in the amount of real coloring matter available. The true logwood tree, from which the best kind of logwood is obtained, is red in color, other trees being deep blue, pale pink, chocolate, yellow, and down to white. These latter trees contain little or no coloring matter, but, according to Drabble and Nierenstein, contain between 6 and 7 per cent. of available tannin matter, and these "bastard" logwoods, as they are termed, being practically equivalent in tannin matter to oakwood and chestnut, are recommended for use in the tannery.

These logwoods are also free from "phlobaphenes," which were the chief cause for the rotting of the East Indian leathers used for bookbinding.

The coloring matter in true logwood is haematoxylin, which becomes oxidized to haematein during the process of "ageing."

It is sold in the form of logwood chips, logwood extract either solid or liquid, or ground or crystallized extract.

There are also haematein, hemolin, etc.; crystals which are logwood extracts prepared and crystallized by special processes.

[1] From the Leather Trades Review.

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Logwood chips are seldom employed at the present time, as they require boiling up several times and for great lengths of time before any reasonable quantity of coloring matter is extracted.

The logwood crystals or haematein crystals find greater favor with the leather dyer, as they simply require boiling with water to dissolve them, and are much more constant in strength. Logwood crystals as a rule are about six times as strong as the chips.

I once had occasion to use logwood chips when dyeing some skins in a factory, thinking to first bottom them with the logwood so as to get a fuller depth of shade of brown on dyeing, but had to give the idea up, as when the logwood, which had been boiled up for about three hours, was put into the paddle it was not found sufficient to even color the skins.

The chief use of logwood on leather at the present time is in the production of blacks, there being no coal-tar black which will give a good black without using about three times the quantity of dye to produce the black than would be required to obtain a commercial shade such as a green or maroon, and it follows that a black so obtained would be rather expensive, whereas the black with logwood and iron is cheap.

There are plenty of good black aniline colors, and practically the whole of them give good blacks upon wool when dyed at the boil, but only dye gray at the temperature at which leather is dyed at. The higher the temperature at which the coal-tar dyes are used the better and deeper is the resulting color.

Logwood and iron give a violet black, and to obtain a dead black it is necessary to add a little fustic to the logwood and a little copper sulphate to the iron, and these four materials are almost exclusively used for the production of blacks upon leather of every description.

When blacks are required upon vegetable tanned leather, such as levant goats, the skins are drummed in logwood or haematein crystals at rate of about 4 ounces per dozen, together with ½ ounce of fustic extract, for 45 minutes. More coloring power is obtained by adding ½ ounce of ammonia, and also helps to cut the grease if there be any present. One ounce of copperas and ¼ ounce of copper sulphate previously dissolved is then added to the drum for not more than two minutes. They are then well washed up in warm water and the black allowed to develop by hanging up. Chrome leather can also be dyed black

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as above where no particular colored flesh is required, but as a general rule the flesh is dyed blue, gray or violet by drumming for a short time with a little of an aniline color.

The skins are then well struck out and folded or pleated down the middle so that the flesh is inside, and tray dyed in first a strong solution of logwood and fustic, and passed through another tray containing iron and copper. For the logwood bath 2 pounds of haematein crystals and 2 ounces of fustic extract and 2 ounces of ammonia for every 10 gallons are a suitable amount. They are allowed to remain in this for about five minutes only, and passed through a solution consisting of 1 pound of copperas and 2 ounces of copper sulphate, being simply passed twice through this bath and not allowed to remain in it. They are then washed in hot water to remove excess of iron, struck out and hung up.

It is also advisable to add a little dissolved soda or ammonia to the logwood when it is dissolved when blacks are being dyed, as some logwoods are slightly acid in character and require this addition of alkali to obtain the maximum amount of coloring matter. Sufficient should be added to turn the logwood violet in color. If the logwood and soda or ammonia are boiled together, the liquor becomes brown and weaker in color.

In the staining of blacks upon heavy leather, the latter is first given a coat of 5 pounds of haematein crystals and ½ pound of fustic, and ½ pound of washing soda for every 10 gallons of stain. This is well brushed on, and followed by an iron liquor of similar strength. The excess of iron is then well washed off. If a little copper sulphate—about one-eighth of the amount of iron used—be added to the iron liquors, a black is produced which is faster to light than would be the case if it were omitted.

There are a few basic coal-tar dyes which, when stained upon leather, give good blacks when used as 1 per cent. solutions, but they do not give quite so good a black as the logwood and iron, and are not so fast to rubbing.

Logwood and iron are also the chief ingredients in the mixtures for the production of blacks upon wool rugs, and are not at all likely to be ousted by any of the coal-tar blacks, which, as previously stated, do not dye black when used below the boiling-point of water.

When logwood is made slightly acid by adding a little formic

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or acetic acid a cheap liquor is made, useful for bottoming skins to be dyed brown or medium greens.

Four ounces of hematein crystals and 1 ounce of formic acid per dozen skins are suitable amounts to use for this purpose. Logwood in this acid condition is also a cheap substitute for annatto for producing the shade known as "London Color," 3 ounces of hematein crystals, 1 ounce of any reddish acid yellow, such as Indian or Cuba yellow, together with 1 ounce of acetic acid, being sufficient for 1 gallon of stain.

Upon alum leather logwood produces a very dark blue or bluish violet, depending upon the amount of alum present, as an excess of alum tends to produce a redder shade. Logwood is always used for the blacking of alum leather for gloves, 10 per cent. of logwood and 2 per cent. of fustic on the drained weight of the skins generally being taken. The skins when thoroughly wet down are drummed in this liquor for one hour, being blacked by passing them through a 1 per cent. solution of an iron salt. Advantage can be taken of this property that logwood has of dyeing blue with alum leather by mordanting any skins that have to be dyed blues or greens or violets by drumming the skins with 2 per cent. alum on the wet weight and then with 5 per cent. logwood crystals. By mordanting with tin chloride instead of alum a purple ground is produced, but the use of tin upon leather is not to be recommended. Some pretty grays can be obtained by dyeing with logwood and iron in the same bath, taking only about one-tenth of the quantity required to dye blacks.

In works where large quantities of logwood are being used continuously it is advisable to test every delivery, and this is best done by having a dye test done. This is carried out as follows:

A piece of cashmere is mordanted with 3 per cent. potassium bichromate on the weight of the wool, commencing cold and raising to the boil during three-quarters of an hour. It is washed and dyed in the same manner with the logwood, taking 15 per cent. if for logwood chips, or 2½ to 3 per cent. of logwood extract, when a good black should be obtained in either case.

Logwood extracts as sold to leather manufacturers are liable to be adulterated with chestnut or any other cheap tanning extract. This can be detected by adding a solution of tartar emetic

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to the dissolved extract, when, if chestnut is present, a flocculent precipitate will be formed, pure logwood giving no precipitate. The use of logwood would be very small in leather factories if there was no such thing as black leather, as all the colors, blue, brown, gray, etc., mentioned above can all be easily produced by means of the coal-tar dyes, although perhaps not quite so cheap.

*Fustic*

Fustic is met with in commerce in the form of a solid extract.

It is used in conjunction with logwood for the production of a dead black, and along with gambier for the mordanting of chrome leather for browns. It can also be used for bottoming browns and greens upon vegetable-tanned leathers.

Upon alum leather it dyes a good yellow, and as it contains very little tannin matter which tightens this class of leather it is generally used as a bottom for all light yellow gloves. It is very little used for ordinary purposes of leather dyeing as the shade produced by fustic can easily be obtained by any of the reddish acid yellows.

*Annatto*

The two chief kinds of annatto that come to England are the Spanish from Brazil and the French from Cayenne. Brazilian annatto occurs in cakes, and has an agreeable odor, whereas the Cayenne variety is a soft paste, and smells rather bad. Its chief use upon leather is for staining the "London Color," which is a pale yellowish brown.

The annatto is diluted with water according to the depth of shade required, and a little chrysoidine or Orange II. is added. The staining must be done cold, as if heated at all some of the many adulterants are liable to be dissolved, and form streaks on the leather. It stains so evenly cold that even boys can be trusted with the staining.

A little dissolved soda or borax is generally added to the annatto, and renders the latter more soluble and redder in colour.

The same shade can be obtained by using a suitable mixture of any reddish acid yellow and a little Orange II., but annatto is likely to be used by stainers for several years, as such beautiful level results can be obtained with it, and, unlike saffron, it is very little dearer than the aniline colors.

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*Turmeric, Weld, Persian Berries, Quercitron Bark, Flavin and Green Ebony*

Turmeric is used as a substitute for saffron, and the shades produced by the remainder are very feeble upon vegetable-tanned leather, but give good shades upon alum leather. They have all been practically superseded by the artificial coloring matters. The best of these yellow dyewoods is Persian berries, which gives a very good yellowish brown upon alum or alum mordanted leather, and a good color upon which to dye any glove color.

Flavin is produced by acting upon quercitron bark with sulphuric acid, and has about 16 times the coloring power of the latter. It is by far the strongest and best of the yellow dyewoods, giving a very good brown shade in conjunction with alum. With a little tin chloride a brilliant reddish yellow is produced. Generally these yellow dyewoods give very poor shades when used alone. With alum leather reddish shades of yellow are produced, with chrome leather greenish yellows.

The brightest shades that can be obtained with them is upon leather which has first been treated with a little tin chloride, and as this substance is detrimental to leather it accounts why these dyewoods are so seldom used at the present time.

With a little iron in the bath greenish shades of black are produced. Green ebony is still used upon leather for some unaccountable reason for greens, as about 10 times the shade produced with it can be obtained with the same weight of Persian berries together with a little iron. Green ebony alone does not dye green but yellow, and to make it dye green a little iron has to be added.

*Brazilwood, Peachwood, Camwood, Barwood, Sanderswood and Madder*

Brazilwood and peachwood are obtained in the form of extracts, and both, as they dye practically the same color, were largely used for mordanting chrome leather when the "ox blood" shade was required a short time ago. Upon alum leather a good crimson shade is produced. When a little tin chloride is added a scarlet similar to cochineal scarlet, but not quite so bright, is obtained. The whole of the redwoods or natural red coloring matters are of no use whatever upon ordinary leather unless the latter be previously treated with some chemical such

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as chrome alum, potash alum, tin chloride or ferrous sulphate.

Camwood, and more especially madder, give very useful shades upon alum leather.

*Orchil or Cudbear*

Orchil is generally bought in a liquid condition, and contains ammonia, and cudbear is orchil liquor evaporated to dryness, containing no ammonia. Dyeing can be done in either an acid, alkaline, or neutral bath, and the latter method is generally employed for the dyeing of maroons for furniture work. It is not fast to light, as generally supposed, but goes on to the leather fairly level. It is generally adulterated with refined logwood extract, as the pure article is by no means cheap for leather dyers.

Other adulterants are small quantities of magenta and methyl violet, and there are even on the market solutions of azo dyes sold as orchil extract or orchil red and containing no real orchil whatever. The chief use of orchil is in the topping of maroons after having been dyed and dried out, and in the dyeing of maroons when a little indigo extract is added. It is better for the leather, to use cudbear than orchil as the ammonia in the latter is liable to weaken the grain.

Cochineal is very seldom used upon leather, because to obtain the best results the leather should be first treated with a mixture of stannous and stannic chloride.

A very brilliant scarlet could be obtained in this way because of the bleaching or clearing effect of the tin salts upon the leather. Almost, but not quite so brilliant scarlets can be obtained by means of the coal-tar dyes if the leather be first cleared with sulphuric acid, then dyed with an acid yellow, and finally with a mixture of orange and scarlet.

The natural dyewoods are still believed by old-fashioned dyers to be the best both as regards coloring power and for obtaining level results, although quite as level results and a greater variety can be obtained with the artificial coloring matters if used judicially.

*Cutch*

Cutch is a solid extract coming from India, and is chiefly used in England as a ground color.

For the re-tanning of Persians, cutch can with advantage be used in place of sumac, as it not only contains more tannin

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matter, but also dyes the leather a good brown and so saves dye. By this means richer and fuller shades can be produced than if the cutch was omitted. Cutch is also used in the place of logwood when staining blacks, and gives a deep dead black very fast to light.

When dyeing Persians which have been stripped and retanned with cutch for glacés, the liquor containing the cutch need not be run off if acid dyestuffs are to be used, and no great harm is done if a little iron liquor is used for toning the shade.

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## PROPOSED METHODS FOR THE DETERMINATION OF THE TOTAL ACIDITY OF TAN LIQUORS

*By H. C. Reed*

*Method I*

The method is based on the precipitation of tannin by an alcoholic-gelatine solution and titration of the filtrate from the tanno-gelatine precipitate with standard alkali, using hematein as an indicator.

The alcoholic-gelatine solution is made by dissolving 10 grams gelatine in 550 cc. water and making to a liter with 95 per cent. alcohol. Care must be taken that the solution is neutral to the hematein. It was found best to neutralize the alcohol and water-gelatine solution prior to combining. If, upon standing, the alcoholic-gelatine solution should jellify, slight warming will be found sufficient to liquefy it.

The hematein should of preference be as pure as possible and a 0.5 per cent. alcohol-water solution (50 per cent. alcohol, 50 per cent. water) was found convenient. To assure a perfectly clear solution it is best to filter. It should be made up fresh each day, as hematein in solution deteriorates rapidly. The amount of the indicator used cannot be specifically stated as this to a measure depends upon the color of the solution to be titrated.

The determination is conducted in the following manner: 25 cc. of the unfiltered tan liquor is pipetted into a stoppered cylinder, graduated to 200 cc. Sufficient of the alcoholic-gelatine solution is added to produce a well defined flocculent precipitate. Water is added to bring the whole to 200 cc. and about 15 grams kaolin added, shaken thoroughly, and allowed to settle.

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The author must here acknowledge his indebtedness to Mr. Eachus of the Yocum-Eachus Laboratory, for the suggestion as to settling out the tanno-gelatine precipitate by the aid of kaolin.

An aliquot portion of the supernatant solution, 25 cc. to 50 cc., is diluted to 200 or 250 cc. and titrated with N/10 NaOH, using the hematein indicator. It is not necessary that the supernatant solution from the tanno-gelatine precipitate should be clear, nor is it imperative that there should be an entire absence of tannin in the solution, as hematein is practically neutral to tannin. If a clear solution is desired the supernatant solution can be run through a filter. With many liquors a sufficiently rapid filtration will be gotten if, after shaking with kaolin, the whole is thrown upon a filter paper.

The proportion of liquor used for the determination may be varied. Liquors containing a large amount of tannin will give better results if less than 25 cc. to 200 cc. are taken, the tanno-gelatine precipitate being less bulky and settling more rapidly after the addition of kaolin. If this is done, it is advisable to pipette larger amounts for titration especially if the liquor is low in acid. With very weak liquors, on the other hand, larger amounts may be taken for the determination. With extremely weak liquors, containing little tannin or color, it is frequently unnecessary to precipitate with the alcohol-gelatine at all, as the original liquor sufficiently diluted will titrate well.

It was found that where a water solution of gelatine or salted solution of gelatine was used, a much bulkier precipitate was obtained and an appreciable loss of acid resulted. When alcohol is used there is perhaps a trifling loss of acid.

It was observed that the alcoholic-gelatine solution gave better precipitation after standing than when freshly made.

The use of hematein as an indicator requires a certain amount of practice. Hematein titrates acetic acid to a purplish-red, gallic acid to a red, and lactic acid to a bluish-red, with soda. In the majority of liquors, the end-point is shown by a change from the yellow which hematein gives in acid solutions, somewhat reddening towards the completion of the titration, with a sudden change to purplish-red at the end-point. It is as stated, entirely a matter of practice and experience to correctly judge when the titration is completed, and the hope is expressed that

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the method will not be condemned if the analyst fails immediately to make successful determinations.

Hematein is affected to a much less degree by salts of gallic acid in the presence of alkalies than is phenolphthalein. In the titration of acetic, lactic and gallic acids and their mixtures, it will give with standard alkali practically the same calculated acid as will phenolphthalein, perhaps a shade less as it is more susceptible to alkalies.

*Method II*

This method is based on the substitution of a basic dye for the alcoholic-gelatine solution and titration of the filtrate with standard alkali, using the hematein indicator.

The basic dyes found serviceable were lemon-yellow "O" (sold by the Berlin Aniline Works) thioflavine F, methyl violet and auramine. Others give correct results in acid but the end-point was not quite so sharp.

It might be presumed that the addition of a basic dye would effect the liberation of free acid from the dye itself, the base of the dye precipitating the tannin. Such, however, does not seem to be the case and apparently very little of the tannin is thrown out of solution. There is, however, precipitated a considerable amount of other matters, largely coloring, and, as stated before, hematein being practically neutral to tannin the estimated acid is correct. Clear filtrates are always obtainable. If methyl violet is used, care must be taken that it is not added either in too great or too little amounts and for this reason the yellow dye, such as thioflavine F, is more serviceable, as it can safely be added in excess. However, the author has found that methyl violet is extremely useful with certain liquors which with a yellow dye give a green instead of a purplish-red end-point, owing to a combination of the hematein indicator with the dye. Practice will enable one to add the methyl violet in correct amount and with many liquors after filtration and dilution, well-nigh colorless solutions will be obtained. It was found that with the majority of liquors by the dye precipitation method, larger amounts could be titrated than with the alcoholic-gelatine method.

Comparative acid determinations by the charcoal, lime, alcoholic-gelatine and basic dye methods show close agreement by

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all but the charcoal method. This method is entirely unreliable and where used according to the official directions, gives, in many instances, filtrates for titration containing tannin which titrates as acid with phenolphthalein. If sufficient charcoal is used to remove all the tannin, much and apparently variable amounts of acid are lost even with the best charcoal, leaving altogether out of the question the fact that different lots of charcoal vary greatly in detannizing, decolorizing and acid-absorbing properties.

The lime method used as Prof. Procter directs, gives good results with the majority of tan liquors, but the titration is tedious and consumes much more time than the proposed alcoholic-gelatine or dye methods.

The author is well aware that hematein is not recommended as an indicator in the titration of organic acids but nevertheless he asserts that it has a decided value in the case of tannery liquors. It might be stated that in addition to hematein, hematoxylin and brazilin were also tested. The former does not work as well as hematein, and the brazilin, although the end-point is sharp, is not of sufficient intensity of color change to make it serviceable.

It is claimed for the methods that they have the advantage of rapidity of execution, combined with accuracy. For this reason they will be found especially valuable in laboratories where a large number of determinations must be made in a short space of time.

The author has been making his own hematein and will gladly furnish samples free of charge to any who desire to examine into the methods proposed.

Results to prove the accuracy of the methods are included in the following tables:

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Solutions were made by extraction of fresh oak and hemlock barks and the acidity determined before and after the addition of an acid solution containing acetic, lactic and gallic acids.

TABLE I.—20 CC. ACID SOLUTION DILUTED TO 200 CC. REQUIRED 3.15 CC. N/10 NaOH FOR 25 CC. TITRATED

| Liquor. | Method. | cc. for analysis. | Dilution, cc. | cc. titrated. | Added acid, cc. | cc. of N/10 NaOH required. | Added acid found in cc. N/10 NaOH. | Actual added acid in cc. N/10 NaOH. |
|---|---|---|---|---|---|---|---|---|
| Oak | Alcoholic | 50 | 200 | 25 | | .15 | | |
| | Gelatine | 50 | 200 | 25 | 20 | 3.10 | 2.95 | 3.15 |
| | Dye | 50 | 200 | 25 | | .40 | | |
| | Lemon-yellow O | 50 | 200 | 25 | 20 | 3.55 | 3.15 | 3.15 |
| Hemlock | Alcoholic | 50 | 200 | 25 | | .15 | | |
| | Gelatine | 50 | 200 | 25 | 20 | 3.10 | 2.95 | 3.15 |
| | Dye | 50 | 200 | 25 | | .40 | | |
| | Lemon-yellow O | 50 | 200 | 25 | 20 | 3.50 | 3.10 | 3.15 |

Liquors were made from extracts of hemlock, oak, chestnut and quebracho, and 25 cc. of each diluted to 200 cc. and the acid determined before and after the addition of a known acid solution as in Table I.

TABLE II.—25 CC. ACID SOLUTION DILUTED TO 200 CC. REQUIRED 2.4 CC. N/10 NaOH FOR 25 CC. TITRATED

| Liquor. | Method. | cc. titrated. | Added acid, cc. | cc. of N/10 NaOH required. | Added acid found in cc. N/10 NaOH. | Actual added acid in cc. N/10 NaOH. |
|---|---|---|---|---|---|---|
| Hemlock | Alcoholic | 25 | | .10 | | |
| | Gelatine | 25 | 25 | 2.30 | 2.2 | 2.4 |
| | Dye methyl | 25 | | .15 | | |
| | Violet | 25 | 25 | 2.50 | 2.35 | 2.4 |
| Oak | Alcoholic | 25 | | .50 | | |
| | Gelatine | 25 | 25 | 2.80 | 2.30 | 2.4 |
| | Dye methyl | 25 | | .50 | | |
| | Violet | 25 | 25 | 2.90 | 2.40 | 2.4 |
| Chestnut | Alcoholic | 25 | | 1.90 | | |
| | Gelatine | 25 | 25 | 4.10 | 2.20 | 2.4 |
| | Dye methyl | 25 | | 2.20 | | |
| | Violet | 25 | 25 | 4.60 | 2.40 | 2.4 |
| Quebracho | Alcoholic | 25 | | .10 | | |
| | Gelatine | 25 | 25 | 2.40 | 2.30 | 2.4 |
| | Dye methyl | 25 | | .15 | | |
| | Violet | 25 | 25 | 2.50 | 2.35 | 2.4 |

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NOTE: 25 cc. of a mixture of equal parts of the above hemlock, oak, chestnut and quebracho liquors with the addition of 25 cc. of the acid solution gave, by the dye method, using methyl violet, 3.1 cc. N/10 NaOH for 25 cc. titrated. The average of the four determinations shown in Table II where the acid was added is exactly 3.1 cc. N/10 NaOH.

A liquor was made by mixing and diluting hemlock, chestnut, oak and quebracho extracts, and 25 cc. of the mixed liquor tested for acid, with and without the addition of a known acid solution containing acetic, lactic and gallic acids, after dilution to 200 cc.

TABLE III.—25 CC. ACID SOLUTION DILUTED TO 200 CC. REQUIRED 3.9 CC. N/10 NaOH FOR 25 CC. TITRATED

| Method. | cc. titrated. | Added acid cc. | cc. of N/10 NaOH required. | Added acid found in cc. N/10 NaOH. | Actual added acid in cc. N/10 NaOH. |
|---|---|---|---|---|---|
| Alcoholic | 25 | | .80 | | |
| Gelatine | 25 | 25 | 4.65 | 3.85 | 3.90 |
| Dye | 25 | | 1.00 | | |
| Lemon-yellow O | 25 | 25 | 4.85 | 3.85 | 3.90 |
| Dye, methyl | 25 | | 1.00 | | |
| Violet | 25 | | 4.90 | 3.90 | 3.90 |

The following table gives results obtained on two tannery liquors and mixtures of equal parts of each, with various basic dyes. The figures represent percentages.

TABLE IV

| Method. | Liquor A. | Liquor B. | 1/2 A. 1/2 B. |
|---|---|---|---|
| Dye, methyl violet | .43 | .28 | .35 |
| Dye, Lemon-yellow O | .42 | .27 | .35 |
| Dye, methyl green | .42 | .27 | .35 |
| Dye, thioflavin F | .42 | .27 | .35 |
| Dye, lemon-yellow II | .42 | .27 | .34 |
| Dye, auramine | .42 | .26 | .36 |
| Alcoholic gelatine | .40 | .23 | .30 |
| Lime (by Procter) | .41 | .27 | .35 |

In the following table results are shown from determination of six tannery liquors by the dye method, with varying quantities of the dye solution, by the alcoholic-gelatine method and the

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lime method of Procter. The dye used was lemon-yellow O in 7 per cent. solution and the results are given in percentages.

TABLE V

| Liquor. | Dye, Lemon Yellow O. | | | | Alcoholic gelatine. | Lime. |
|---|---|---|---|---|---|---|
| | 10 cc. | 5 cc. | 2½ cc. | 1 cc. | | |
| 1 | .29 | .29 | .29 | .29 | .28 | .25 |
| 2 | .27 | .26 | .27 | .27 | .23 | .23 |
| 3 | .46 | .46 | .46 | .48 | .46 | .50 |
| 4 | .59 | .59 | .60 | .61 | .60 | .47 |
| 5 | .49 | .49 | .50 | .51 | .48 | .50 |
| 6 | .77 | .77 | .77 | .77 | .77 | .76 |

NOTE: In the determinations shown in the above table where the dye was used, 50 cc. of the liquor was taken diluted to 200 cc. and 25 cc. of the filtrate titrated. A mixture of equal quantities of the six liquors gave by the dye method, .48 per cent. acid and the average of all six determined separately by this method is exactly .48 per cent.

## REVIEWS

**Contribution to the New International Method of Tanning Analysis.** K. SCHORLEMMER AND H. SICHLING. *Collegium*, 1907, 288, 435.—The authors compared the old filter method with the new shake method and they give the results of a large number of analyses made by both methods. With pure liquid quebracho extracts the difference in the percentages of the non-tannins between the two methods is very slight, increasing slightly with the solid extracts but is greater when the extract has been chemically treated. This was particularly shown when mixing pure quebracho extract with different amounts of grape sugar and sodium bisulphite. It was noted that with these extracts and also with mimosa mixed with sulphite, that the residues from the filter method were colored slightly green and contained small amounts of chromium oxide. This was not noticed with the shake method, possibly on account of the residues being intensely colored. Three samples of chestnut extract from the same manufacturer which appeared from the color of their foam to be different, gave with the filter method 9.45, 9.40 and 9.55 per cent. of non-tannins, but showed with the shake method 10.70, 11.60 and 12.05 per cent. of non-tannins, these results being in the same order as the increase in the color of the extracts. Pine and hemlock extracts showed considerable differences from the filter method. Solid myrabolam extract, which had only been taken on account of its high non-tannins, showed a difference of 5.10 per cent., which is not so very high. Gambier showed a remarkable large difference. The results on a chemically prepared sumac extract showed some variation similar to a decolorized and sulphited maletto extract. The difference in the coloration of the chromed hide-powder by mimosa and

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mangrove extracts is very pronounced, especially in the shake method. With mangrove, which contains a considerable amount of coloring matter, the differences are greater, with the decolorized mangrove they are not as large. The differences with oak are very small, valonia being considerably greater. The results obtained on sapped liquors showed good concordance and can be considered very useful. An interesting thing to note is that a chestnut extract gave the same difference between the two methods before and after addition of grape sugar. This would indicate that an extract containing high non-tannins and to which more non-tannins have been added does not influence the filter method, the differences remaining constant. In closing, the authors state that the results show that when using the filter-bell with the slightly chromed hide-powder of the German Experiment Station of Leather Industry good concordant results are obtained but which show too high tannin, and which are not in accordance with the practical experience of the tanner. The results of the shake method also show good concordance and although in this method non-tannins are absorbed, but in smaller amounts, the method yields more valuable and reliable results and the authors consider they have proven the same to be the more correct results.

**Japan Leather and Its Manufacture.** W. EITNER. *Der Gerber*, 1907, 799, 337.—Japan leather resembles alum leather in appearance and is principally used for articles of clothing, being often preferred in place of the latter on account of its greater strength, but principally because it does not affect metals covered with the same when perspiration acts upon it, as is the case with alum leather, and also preserves the dye well without fading. The leather is neither tanned with alum nor with any tannin and can simply be considered prepared raw hide. Mr. Fried Reinhart states that the Japan leather imported into Europe is produced in a single village called Jacayimura near the city of Himeji, the total yearly production being 50 to 60,000 sides, the entire population of the village being occupied in its manufacture. The hides used for the leather consist principally of Corean and Chinese oxen and cow hides. The spring and fall is considered the best time for the tanning and the raw hides are hung in a mountain stream of clear, clean water, called the Ischakawa, to soak and according to the time of the year and temperature conditions, they remain there from 1–3 weeks until ready for unhairing. They are then unhaired and cleaned with a small blunt knife, the sides are spread out on the ground, salt is strewn upon them, they are allowed to remain there from 24–48 hours after which they are slowly dried, exposing the flesh and grain sides alternately to the sun. The dried sides are then softened in the water from 10–15 minutes and each side oiled on both sides with about 200 grams of rape oil, allowing the oil to soak in. They are then worked with the knees and again dried in the sun, after which they are again worked. The dried leather is again softened in the water, which removes the salt, again slowly dried in the sun, and again worked. This procedure is continued several times. The length of the tanning is supposed to take from 2–4 months. As this leather is produced in Jakayimura only the action of the water of the stream there is believed to be the cause. Leather is

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tanned from start to finish in the open on the stony banks of the stream, the finishing taking place in the houses of the inhabitants of the village. Experiments have been made above and below the village to produce the leather, but without success, which tends to indicate that just at this place an alum bed is under the river. The author states that samples of this leather which he obtained contained no tannin and only 5 per cent. of liquid fat of which about 1.5 per cent. was natural hide fat and the balance a non-drying vegetable oil which has no tanning property. The leather is consequently only raw hide and also acts as such on boiling, dissolving into glue, although differing from raw hide by not plumping in water, being less liable to putrefaction and not becoming like raw hide on drying. The author states it is a well-known fact that hides which have been sunburnt are difficult to soften on soaking and sometimes cannot be softened at all. The author considers this the foundation of the manufacture of Japan leather, and nothing can be ascribed to the action of the water at the village but only to the favorable location of the village in regard to sun. Similar conditions of the hide can be produced with alcohol or alcohol-ether or formaldehyde, and the author gives the following procedure: The unhaired and cleaned hides are placed in strong denatured alcohol to which has been added 5 per cent. on the weight of the hides of castor oil which readily dissolves in the same. The hides are allowed to remain there from 4–8 days and the vessel should be tightly closed in order to prevent the evaporation of the alcohol. The leather is then taken out and allowed to dry and is then finished. As alcohol is expensive the above process is of little practical value. The author has worked out another process for producing this kind of leather in which the cleaned and unhaired hides are hung in a formaldehyde solution containing 1 part of formaldehyde in 100 parts of water. After 5 days ½ part of formaldehyde per 100 parts of water are added and the hides kept there from 6–8 days longer. By taking out small samples of the hides and drying the same it can be determined when they are finished. When finished the hides are rinsed and then wheeled for one hour with a 3 per cent. solution of a neutral oil soap, after which they are washed. In case it is desired to have the leather very soft, 1–1.5 per cent. of olive or castor oil is added to the soap solution. The washed leather is dried and placed in moist sawdust until sufficiently moist for finishing. In order to heighten the white color of the leather talcum or white zinc can be applied. Naturally such leather must be sold by measure and not by weight.

**On the New Method of Tannin Analysis.** '*Der Ledermarkt*, 1907, 99, 8.— A large number of analyses, comparing the old filter method with the new shake method, were carried out in the laboratory of the leather works of Doerr & Reinhart at Worms a. Rh., Germany, and showed that more non-tannins are absorbed in the old method than in the new method. The firm states that the results obtained by the old method are worthless to the tanner and that under no consideration would they buy extracts based on the old method but would demand guarantee by the new official shake method of the I. A. L. T. C.

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**The Solution of Extracts.** W. EITNER. *Der Gerber*, 1908, pp. 1–2, 15–17, 31–3.—The principal ingredients of quebracho extract may be divided into tanning and dyeing substances, resins and non-tanning. The most important component which may be called the light colored tannin of quebracho is of a reddish-yellow color, easily soluble in cold water and has great tanning power, penetrating the fibers of the hide. The second component is reddish brown, difficultly soluble in cold water and only completely soluble at 40° C; it also tans, but acts on the surface of the fibre, having little penetrating power and serves to give body to the leather. It may be called the colored tannin of quebracho. The dyestuffs, which are strongly colored, first dissolve at 70° C. and therefore cannot act in the tanning process; they may be used however as filling material between the fibers and make the leather stiff and heavier. The resins of quebracho wood are extracted under pressure at 100° C. upwards; they do not act upon hide fibre but may be deposited in lumps and stains, especially upon the flesh side. The boundary between the dyestuffs and resins is not a sharp one.

The ingredients of mangrove extract are much more soluble and do not deposit on cooling; their tanning power however is much inferior.

The tannins of myrabolams dissolve easily but it is difficult to obtain clear extracts because of decomposition of other bodies present.

Maletto tannin dissolves easily and deposits little on cooling. Added to quebracho the solubility and tanning power are increased.

The solubility of quebracho extract may be increased by treating the extract concentrated to 25° Bé. with sodium bisulphite under pressure at high temperatures up to 150° C. The colored tannins become soluble in cold water, lighter in color, but they now resemble the light colored tannins in their action, penetrating the fiber and no longer rendering the leather dense.

The less soluble components of extracts, especially quebracho, may also be rendered more soluble by alkaline treatment; the colors become however darker and the tanning power is lowered.

Easily soluble extracts can also be made by settling and removing the less soluble material before concentration. This yields a superior but expensive extract.

A liquid extract may be considered technically soluble if it may be diluted at will with water at 25–30° C. to clear solution. In practice, so-called cold-soluble solid extracts are dissolved hot, but the diluted solutions should separate little deposit on cooling to 19° C.

Commercial quebracho extracts may be tested in accordance with the solubility conditions outlined in the first paragraph. The extract is dissolved and cooled to the temperature suitable for the particular effect desired, namely, 20° C. for purely tanning ingredients, 40° C. for tanning and swelling, and above 40° C. for merely filling. The author cites a series of typical analyses of this sort.

Such experiments show that with pure quebracho extract, the greater part of the sediment separates at temperatures between 20° C. and 40° C.; this consists exclusively of the colored tannins and may be utilized to give the leather body and weight by tanning at higher temperatures up to 40° C.

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The resinous ingredients of the extract which are without action in tanning may be utilized in weighing sole leather by the "burning-in" process (Einbrennen), where the tanned hide is saturated with the extract up to 75° C.

In practice, quebracho extract is often used in mixture with others, especially oak and chestnut-wood extracts; it is thought the solubility ratios of the quebracho extract are thereby improved.

Solubility determinations are also detailed by the author, showing the smaller amounts of sediment obtained from chestnut and oak-wood extracts and also an extensive series of similar experiments with mixtures of the same with quebracho extracts. These show that chestnut-wood extract increases the solubilities of all the ingredients of quebracho while oak-wood extract increases the solubility only of the easily soluble ingredients, while that of the resins is decreased.

Many tanners judge extracts by the amount of sediment left from solutions. The author points out that adulterated extracts judged in this way show the most favorable results, while pure quebracho extract gives the maximum sediment.

In conclusion, the following practical precepts are deduced. All extracts, also "cold-soluble," liquid or solid should be dissolved hot. Mixtures should be made before solution. Extract solutions for tanning light leathers should be cooled to 30° C. and settled. The sediment can later be dissolved by blowing in steam, the solution cooled to 75° C. drawn off from the separated resin and employed for weighting and filling. The renewal of the vat solutions with fresh extract which has not been settled is not so rational, as it causes a premature filling of the pores of the hide and arrests the tanning. It is better to tan with a weak but resin-free liquor which produces more uniform results and to finish with stronger extracts if heavy weighted and stiff leather is desired. The after-tannage can be completed at 62° C., a temperature which tanned leather will withstand completely.

**Analysis of Oak-Wood Extract According to the New Official Method.** JAN JEDLICKA. *Collegium*, 1908, pp. 14–20.—A description is given of a series of comparative tests made upon the product of the Mitrovitz extract factory.

As a mean of 50 analyses the shaking method gave 1.7 per cent. higher non-tannins than the filter method (average non-tannins = 17 per cent.). Two preparations of hide powder were used (I) from Mehner and Stransky (II) from the Freiberg Versuchsanstalt which gave about equal results.

*Solubles in Chromed Hide Powder.*—As a means of 10 blank tests with pure water according to the new method, both hide powders yielded 1.0 per cent. non-tannins. The author recommends a correction should be made for solubles in chromed powder, preferably not a constant, but determined at the time used, since the amount may change with time. The storage of non-chromed powder in tin boxes is preferred to that in bottles with ground stoppers. The solubles above found required in 50 cc. of filtrate 0.3 cc. N/10 $AgNO_3$ corresponding to 0.26 per cent. non-tannins (as NaCl). Attempts to more completely wash the chromed powder failed. Parallel

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analyses of extract both with and without a preliminary shaking of the chromed powder with water gave the same results, showing that the tannin solutions remove the solubles of the powder as well as pure water.

*Influence of Time of Shaking.*—Ten experiments showed a mean of 0.6 per cent. *increased* non-tannins on continuing the shaking to one hour.

*Influence of Amount of Chromium.*—The author points out a lapse in the official formula of 2 grams crystallized chromium chloride to 100 grams of dry powder; this would give the powder only 0.4 per cent. Cr while the commission prescribes for limits 0.5–2.0 per cent. A series of analyses made with powders of varying chromium content gave

| | | | | | |
|---|---|---|---|---|---|
| Non-tannins..... | 16.6 | 15.2 | 14.9 | 14.8 | 14.8 |
| Cr..... | 0.4 | 0.8 | 1.2 | 1 6 | 2.0 |

It is, therefore, recommended that a chromium percentage of 1–1.5 be employed as giving more constant results.

**Comparative Tannin Analyses.** KARL SCHORLEMMER. *Collegium*, 1907, p. 447.—The author gives the results of parallel analyses of various barks and extracts by the old and the new methods, the differences being slight; the new method is preferred for its convenience.

**The Wattle Industry of Natal.** *Journal of the Society of Arts*, 1908, 304.—The black wattle tree was transplanted from Australia, and when first introduced into Natal there was no idea of its becoming a valuable commercial asset, but its beauty, combined with its quick growth, made it a particularly desirable tree for ornamental purposes, and with this object in view its growth was first begun in Natal a little over a quarter of a century ago. It may be taken that the commencement of the cultivation in Natal of wattle plantations dates from the year 1888. From about that period the wattle was intelligently and systematically planted and grown, until in 1906 the acreage in wattle plantations in Natal was 80,762 acres, and this acreage was probably increased in 1907. Wattle bark has now attained to third place in the list of oversea exports from the colony, and there is every indication of a continued increase in the output. The wattle industry gives a quick return, beginning about five years after the tree is planted. The tree needs no replanting, it being a perennial, which the cutting of the first planting does not interfere with. According to the American Consul at Durban, 39 sample packages were sent to London in 1886, and were followed next year by 447 packages. The encouraging and satisfactory reports received from these shipments—which continued to be made in packages until 1896—gave great confidence in the future of the business, and the plantations increased their production considerably. From this modest beginning the output and shipments increased gradually until 1895, when 57,666 packages were shipped. The industry passed through its experimental stages during this period, in which was shipped a total of 168,193 packages, valued at £60,000. There were shipped in 1896 3,378 tons, in 1898 9,427 tons, and in 1902 35,537 tons. In 1904 the shipments were valued at £91,000, in 1905 at £100,000, and in 1906 at £89,000. For the ten months ended October, 1907, they were valued at £125,000. The trees are felled and stripped

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of their bark gradually after they are five years old. Complete felling will probably take place when the trees are ten years old. The average yield is estimated at half a ton per acre each year. In addition to the bark the wood is valuable when there is a demand for this kind of timber. The cutting must take place when the sap is up, which is between January and August The bark is then stripped from the entire tree, extending to all limbs of two inches in diameter. The bark in this form is dried; many plantations have large sheds in which to dry it, though sometimes, when the weather is fine, it is dried in the open. When it has become dry—which should occur after twenty or twenty-five days—it is prepared for market, by being ground, cut, or shredded into small bits. It is then packed in bags of about two hundred pounds each, and is ready for export. To prospective buyers a word of warning is, says the Consul, necessary, because some farmers do not take the proper care in curing their bark, and when it reaches the European market it is dark, mildewed, and otherwise damaged; and it has been said that some unscrupulous persons have at times mixed other barks with the wattle. The destination of the bark exported from Natal in the year 1906 was as follows, the countries being given in the order of their importance from the point of view of consumption: United Kingdom, Germany, Russia, Austria, Belgium and Mauritius. The quality of the wattle grown in Natal is equal to that produced anywhere, and analyses have shown it to contain as much as 40 per cent. of tannin. At the present time there seems to be no serious competitor to Natal wattle bark, its cultivated and increasing supplies going far to meet the naturally grown and diminishing supplies from the original home of the tree. In the districts of Griqualand and Pondoland in Cape Colony, cultivation of the wattle has been systematically undertaken, but the adaptability of those districts to its growth has not yet been proved. In German East Africa experimental tests have also been made, and bark from there, upon being analyzed at Hamburg, has shown from 27–41 per cent. of tannin.

## PATENTS

**Bark-Peeler: U. S. Patent No. 875,849** to G. R. RISHEL and E. H. WYKOFF, Alexandria, Pa. An improved bark-spud, or tool for removing bark from trees.

**Process of Manufacturing Condensation Products from Tannin, Formaldehyde, and Aromatic Monohydroxyl Compounds: U. S. Patent No. 876,311** to H. HILDEBRANDT, Halle, Germany. A process for manufacturing the above products, as for example the condensation product of thymol with formaldehyde and tannin, which product is soluble in water, soluble in alcohol, soluble in alkali, and melts with decomposition at about 235° C. The method claimed for making this specific product, is to mix an alcoholic solution of thymol with an aqueous tannin solution, in substantially molecular proportions, adding 40% formaldehyde largely in excess of the theoretical quantity; pour the mixture thus obtained into a great excess of concentrated hydrochloric acid, separating the precipitate formed, and then wash and dry the precipitate.

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**Process of Tanning: U. S. Patent No. 876,583** to G. H. PENDLETON, Busch, Oklahoma. The hides are prepared in the beam house as usual, and then given a bath in an alkaline solution of gum gambier. After a period, gum arabic, oil of hops, and extract of wild-cherry are added to the bath. The hides remain in this mixture until tanning is complete.

**Gage for Skiving Machines: U. S. Patent No. 876,772** to M. CAVANAGH, New York, N. Y.

**Art of Finishing Surfaces of Heels, Soles, Etc.: U. S. Patent No. 876,861** to W. W. CROOKER, Lynn, Mass. Consists in applying a preliminary coating containing wax in emulsion and an alkaline solution of coloring matter, and then applying a finishing coating containing alcohol and other ingredients to make the finished surface waterproof and strengthen the color.

**Process of Tanning Hides and Skins: U. S. Patent No. 877,341** to J. INOUYE and T. DOGURA Kawakami, Japan. A preparatory treatment of a bath composed of a solution of ferrous sulphate, potassium nitrate and potassium bichromate.

**Process for Making Vegetable Extracts: U. S. Patent No. 877,660** to J. MEIKLE, Glasgow, Scotland. A continuous process of obtaining extracts from vegetable matters, consisting in evaporating a solution of extract in a vacuum, drawing under a vacuum the vapors from the solution through said matters so as to cause the vapors to condense thereon, drawing off by suction a fraction of the condensed vapors containing fresh extract in solution, and forcing the condensate to flow under the action of air pressure to rejoin the first-mentioned solution.

**Manufactured Leather: U. S. Patent No. 878,485** to A. W. CASE, Highland Park, Conn. A sheet of leather board formed from leather pulp material, and after being formed and dried treated to a bath including rosin and heated mineral oil.

**Process of Decolorizing Tannic Extracts: U. S. Patent No. 878,618** to L. DUFOUR, Genoa, Italy. A process of decolorizing extracts, which consists in adding thereto a reducing agent comprising in separate combinations the sulphurous acid radical and the phosphorous acid radical, said reducing agent being associated with formaldehyde, adding thereto an acid capable of displacing the said radicals and heating the mixture.

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## THE ACIDITY OF TAN LIQUORS

*By J. W. Phelan and P. S. Fiske*

The methods now in general use for the determination of the acidity of tan liquors (the official or bone-black method, the gelatin method, and the quinine method) are not entirely satisfactory, nor are the results obtained by the different processes concordant. Believing that the method ordinarily employed

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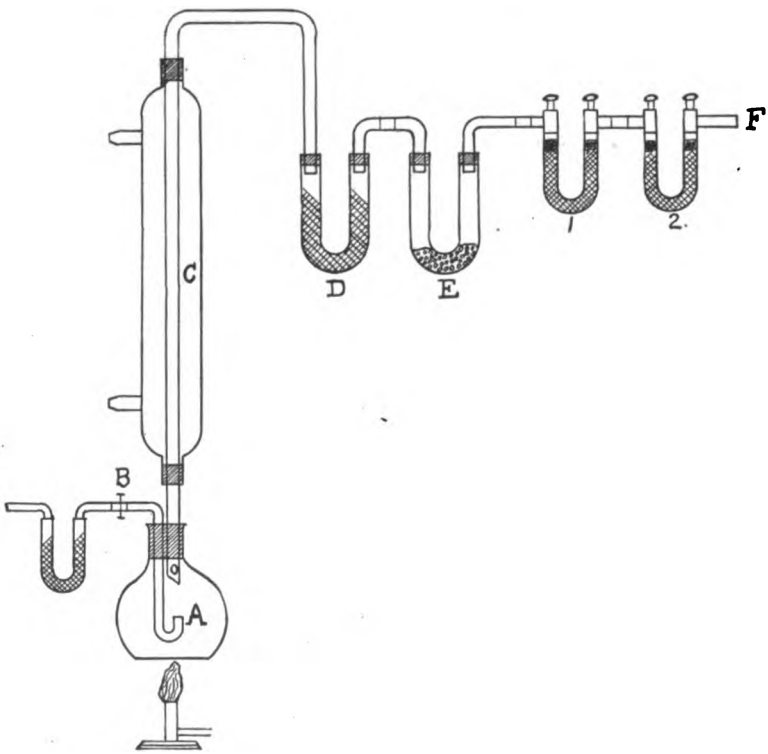
to determine carbon dioxide in carbonates could be so modified as to be available for determining this acidity, the following procedure has been devised and tested:

50 cc. of the liquor are placed in the 150 cc. extraction flask "A" with 2 grams of calcium carbonate. The mixture is then boiled, the pinch-cock "B" being closed, and the water vapor and carbon dioxide evolved pass through the condenser "C,"




where the steam condenses, then through the two drying tubes "D" and "E," containing calcium chloride and sulphuric acid, respectively, which remove the last traces of the water vapor. Finally, the carbon dioxide remaining, passes into the two soda-lime tubes "1" and "2" where it is absorbed.

The end of the inlet tube in "A" is turned up to prevent the escape of bubbles of carbon dioxide. Silver sulphate is added to the sulphuric acid in the drying tube to prevent the carrying over of any hydrogen chloride gas formed in the calcium

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chloride. The best form of absorption tubes for the purpose are those provided with ground glass stop-cocks. These contain, in the arm farthest from the apparatus, a layer of calcium chloride about 1 inch long, to absorb any water formed by the action of carbon dioxide on the soda-lime. The calcium chloride tubes and all soda-lime tubes are provided with cotton plugs at both ends to prevent the mechanical carrying away of fine particles.

When the mixture in the flask has been boiled a sufficient length of time (this was found to be five minutes) the lamp is removed, pinch-cock "B" opened, and suction attached at "F." The air drawn in passes through the soda-lime tube "G," where all carbon dioxide is removed, bubbles through the liquid in the flask, and sweeps all the carbon dioxide remaining in the flask and drying tubes into the absorption tubes. These tubes are then removed, allowed to stand in the balance case twenty minutes, weighed, and the increase in weight reduced to per cent. of acid, as acetic, by multiplying by the factor 5.454. $2HC_2H_3O_2:CO_2 = 120:44$. As only 50 cc. were used this becomes $120:22 = 5.4521$.

To determine the general accuracy of the method, and detect possible sources of error, blank tests were run as follows:

(1) The change in weight of the two soda-lime tubes when 100 cc. of water was boiled in a flask for thirty minutes, and the current of air drawn through for thirty minutes more, was noted. The average change in weight was found to be less than 0.001, and the actual difference in weights of the two tubes after a series of seven tests was only 0.0013. This seems to indicate that for a run of one hour (more than twice the time subsequently used in the analysis of yard liquors) the error should not be more than 0.001. As the tubes could not under ordinary conditions be weighed to an accuracy of more than 0.0005 this error is unimportant.

(2) A set of potash bulbs was substituted for the soda-lime tubes, but the results were less satisfactory, and the manipulation more difficult. On six tests the bulbs changed on the average 0.0015. When, in two cases, a soda-lime tube was added beyond the bulb, it gained in one case 0.0003 and in the other nothing.

(3) 2 grams of pure calcium carbonate were added to the water

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and the mixture treated as before. The total gain was 0.0012.

(4) 50 cc. of a standard solution of a mixture of lactic and acetic acids were added to 2 grams of calcium carbonate. This acid was standardized against decinormal sodium hydroxide, which had been accurately standardized against oxalic acid. The factor of the mixed acids was found to be 0.0727 N. Hence, 50 cc. would be equivalent to $0.0727 \times 1.1$ or 0.0800 gram of carbon dioxide. Calculated as acetic acid the acidity of this solution was 0.436 per cent. The following results were obtained:

TABLE I

| | Time. | | Weight of carbon dioxide. | | | | |
|---|---|---|---|---|---|---|---|
| No. | Boiled, min. | Air, min. | Tube 1. | Tube 2. | Total. | Per cent. of acid. | Per cent. theoretical. |
| 1 | 25 | 30 | 0.0781 | 0.0016 | 0.0797 | 0.435 | 99.6 |
| 2 | 27 | | 0.0782 | 0.0010 | 0.0792 | 0.432 | 99.0 |
| 3 | 25 | 63 | 0.0765 | 0.0017 | 0.0782 | 0.427 | 97.8 |
| 4 | 10 | 21 | 0.0793 | 0.0002 | 0.0795 | 0.433 | 99.4 |
| 5 | 10 | 20 | 0.0771 | 0.0009 | 0.0780 | 0.425 | 97.4 |
| 6 | 10 | 20 | 0.0401 | 0.0394 | 0.0795 | 0.434 | 99.4 |
| | | | Average per cent. of acid | | | 0.431 | |
| | | | Average per cent. of theoretical | | | 98.7 | |

It should be noted that No. 6 shows that an accurate result is obtained even when one tube is nearly exhausted.

Another solution of mixed acids subsequently prepared, and standardized as above, gave the following results: (The factor in this case was 0.0739 N and the equivalent weight of carbon dioxide was 0.0813. The acidity of this solution was 0.443 per cent.)

TABLE II

| | Time. | | Weight of carbon dioxide. | | | | |
|---|---|---|---|---|---|---|---|
| No. | Boiled, min. | Air, min. | Tube 1. | Tube 2. | Total. | Per cent. of acid. | Per cent. of theoretical. |
| 1 | 5 | 20 | 0.0795 | 0.0006 | 0.0801 | 0.437 | 98.5 |
| 2 | 5 | 20 | 0.0798 | 0.0000 | 0.0798 | 0.435 | 98.1 |
| | | | Average per cent. of acid | | | .436 | |
| | | | Average per cent. of theoretical | | | 98.3 | |

(5) 50 cc. of acid were treated with 2 grams of calcium car-

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bonate in the cold and air was drawn through for about one hour. The weight of carbon dioxide obtained was only 0.0073, or nine per cent. of the whole.

From the results of these tests it was evident: (1) that an accuracy in weighing greater than 0.001 could not be expected; (2) that the best method for absorbing the carbon dioxide was by the use of two soda-lime tubes; (3) that practically no carbon dioxide was given off from a solution of calcium carbonate under these conditions; (4) that calcium carbonate treated with acid in the cold evolved carbon dioxide so slowly that it was possible to add the acid to the carbonate, before connecting the flask to the rest of the apparatus, without introducing any error through loss of carbon dioxide, and that for the same reason the solutions must be boiled to obtain the carbon dioxide quantitatively; (5) that the time of this boiling could be reduced to five minutes, and that it was unnecessary to draw air through for more than twenty minutes. Doubtless, the carbon dioxide would have been drawn out more readily if air had been bubbled through during the boiling, and in every case where the boiling lasted more than ten minutes, suction was attached at the end of this time. During the first ten minutes, however, the frothing of the liquid, and the unequal pressure, owing to rapid and irregular liberation of carbon dioxide, rendered it inconvenient to have the pinch-cock "B" open.

Samples of yard liquors were obtained and tested, with the results shown below. These liquors were analyzed at the tannery by the gelatin method, and these results also are given in the table. In each case 50 cc. of the liquor and 2 grams of calcium carbonate were used.

TABLE III.

| No. | Time. Boiled, min. | Time. Air, min. | Weight of carbon dioxide. | Per cent. as acetic. | Per cent. by gelatin method. |
|---|---|---|---|---|---|
| 1 | 10 | 20 | 0.0401 | 0.219 | 0.25 |
| | 10 | 20 | 0.0378 | 0.206 | |
| 2 | 10 | 20 | 0.0695 | 0.379 | 0.43 |
| | 12 | 18 | 0.0677 | 0.369 | |
| | 10 | 20 | 0.0726 | 0.396 | |

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TABLE III (*Continued*)

| No. | Time. Boiled, min. | Time. Air, min. | Weight of carbon dioxide. | Per cent. as acetic. | Per cent. by gelatin method |
|---|---|---|---|---|---|
| 3 | 11 | 20 | 0.0628 | 0.342 | 0.42 |
| | 10 | 20 | 0.0643 | 0.350 | |
| | 10 | 20 | 0.0657 | 0.358 | |
| 4 | 5 | 20 | 0.0616 | 0.336 | 0.40 |
| | 5 | 20 | 0.0617 | 0.337 | |
| | 10 | 20 | 0.0691 | 0.377 | |
| | 10 | 20 | 0.0689 | 0.376 | |
| 5 | 5 | 20 | 0.0497 | 0.271 | 0.263 |
| | 5 | 20 | 0.0462 | 0.252 | |
| | 5 | 20 | 0.0471 | 0.257 | |
| 6 | 5 | 20 | 0.0533 | 0.291 | 0.436 |
| | 5 | 23 | 0.0550 | 0.300 | |
| 7 | 5 | 20 | 0.0546 | 0.298 | 0.461 |
| | 5 | 21 | 0.0533 | 0.291 | |
| 8 | 5 | 20 | 0.0850 | 0.464 | 0.486 |
| | 5 | 20 | 0.0735 | 0.401 | |
| | 5 | 20 | 0.0792 | 0.432 | |
| 9 | 5 | 20 | 0.1280 | 0.698 | 0.507 |
| | 5 | 20 | 0.1204 | 0.657 | |
| | 5 | 20 | 0.1234 | 0.673 | |

It is seen that the results are in each case, except No. 9, lower than those obtained by the gelatin method by at least 5 per cent., which is apparently more than the limit of error of this process. Further, it is seen that a reduction in the time of boiling from ten minutes to five minutes brings about (No. 4) a reduction of 11 per cent. in the weight of carbon dioxide obtained. The corresponding reduction when pure acid was used is shown by Tables I and II to have been only 0.4 per cent., while a reduction of time from twenty-five minutes to ten minutes gave only 0.3 per cent. less; hence, it appears that since five minutes boiling is sufficient to allow the free acid to liberate more than 98 per cent. of the equivalent weight of carbon dioxide, the increase obtained on further boiling must be carbon dioxide set free by acids formed in the breaking down of the tannin, or some other constituent of the liquor.

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The following tests were next made to determine whether this breaking down really occurs in a case of tannin and also to determine if it increased proportionately with the length of time of the boiling.

(1) A sample of pure tannin was boiled with 100 cc. of water with the following result:

TABLE IV

| Time. | | | |
|---|---|---|---|
| Boiled, min. | Air, min. | Weight of tannin. | Weight of carbon dioxide. |
| 30 | 30 | 0.2551 | 0.0031 |

This seems to show that small quantities of carbon dioxide are liberated by the decomposition of tannin. To find out whether the tannins reacted with the carbonate to liberate carbon dioxide, four samples of pure tannin, weighing each about 0.25 gram, and one sample of solid extract were added to 50 cc. of water and 2 grams of calcium carbonate and boiled for one-half an hour with these results. (In the fifth column is given the acid equivalent of the tannin calculated as acetic.)

TABLE V

| Time. | | | | |
|---|---|---|---|---|
| Boiled, min. | Air, min. | Wt. of tannin. | Wt. of carbon dioxide. | Per cent. of acid. |
| 30 | 30 | 0.2536 | 0.0273 | 59 |
| 30 | 15 | 0.2536 | 0.0245 | 53 |
| 30 | 30 | 0.2541 | 0.0243 | 52 |
| 30 | 30 | 0.2545 | 0.0261 | 56 |
| 28 | 32 | 0.5037 (extract) | 0.0084 | 9 |

(3) A sample of extract was heated with 50 cc. of water and 2 grams of calcium carbonate repeatedly, air being drawn through each time, in order to study roughly the progress of the decomposition. The sample was allowed to stand for some time in the cold between weighings as indicated in the first column.

TABLE VI

| | Time. | | | |
|---|---|---|---|---|
| Standing, hrs. | Boiled, min. | Air, min. | Wt. of extract. | Wt. of carbon dioxide. |
| | 45 | 22 | 0.5086 | 0.0111 |
| 18 | 74 | 13 | | 0.0073 |
| 6½ | 31 | 15 | | 0.0034 |
| 19 | 45 | 45 | | 0.0032 |
| 3 | 44 | 58 | | 0.0045 |

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Hence, it is evident that the decomposition proceeds rapidly with heat. This conclusion was confirmed by the following titrations of pure tannin with decinormal sodium hydroxide. In each case an excess of alkali was added and the solution finally neutralized with decinormal hydrochloric acid, with litmus as an indicator.

TABLE VII

| Wt. tannin. | Time boiled, min. | NaOH. | HCl. | Excess NaOH. |
|---|---|---|---|---|
| 0.2529 | | 12.84 | 12.14 | 0.70 |
| 0.2522 | 30 | 41.45 | 29.15 | 12.30 |
| 0.2551 | 45 | 50.19 | 30.43 | 19.76 |

(4) To determine whether this decomposition continues rapidly after the mixture has been cooled, a solution of about 0.25 gram of tannin in 50 cc. of water, with 2 grams of calcium carbonate, was heated thirty minutes, air was drawn through for thirty minutes, and the tube was weighed; air was drawn through again, this time for twenty minutes, and a second weight taken; air was again drawn through for twenty minutes and a third weight taken. Another sample was similarly treated, except that it was allowed to stand one day between the first and second weighings, and four days between the second and third.

TABLE VIII

| Time. | | | | | |
|---|---|---|---|---|---|
| Standing, hrs. | Boiled, min. | Air, min. | Wt. tannin. | Wt. $CO_2$. | Total per cent. of acid as acetic. |
| | 30 | 30 | 0.2545 | 0.0264 | 57 |
| 38 | | 20 | | 0.0014 | 60 |
| 29 | | 20 | | 0.0006 | 61 |
| | 30 | 30 | 0.2592 | 0.0265 | 56 |
| 18 | | 40 | | 0.0078 | 72 |
| 96 | | 31 | | 0.0126 | 99 |

Hence the decomposition does go on in the cold, although but slowly.

These tests demonstrate that the error introduced by boiling a solution of tannin, or by allowing such a solution to stand for any great length of time is considerable. To determine the extent of error introduced in this process by ten minutes and also by five minutes boiling, with varying percentages of

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tannin, liquors of known constitution were prepared of 50 cc. of the mixed lactic and acetic acids and varying amounts of tannin. The acid in these was determined with the following results:

TABLE IX

Time: Boiled, 10 min. Air, 20 min.

| Per cent. of tannin. | Wt. of $CO_2$. | Wt. $CO_2$ due to acid. | Excess wt. of carbon dioxide. |
|---|---|---|---|
| 2 | 0.1406 | 0.0800 | 0.0606 |
| 2 | 0.1377 | | 0.0577 |
| 4 | 0.1806 | | 0.1006 |
| 4 | 0.2254 | | 0.1454 |

TABLE X

Time: Boiled, 5 min. Air, 20 min.

| Per cent. of tannin. | Wt. of $CO_2$. | Wt. $CO_2$ due to acid. | Excess wt. of carbon dioxide. |
|---|---|---|---|
| 1 | 0.1044 | 0.0813 | 0.0231 |
| 1 | 0.1070 | | 0.0257 |
| 1 | 0.1101 | | 0.0288 |
| 2 | 0.1313 | | 0.0500 |
| 2 | 0.1331 | | 0.0518 |
| 3 | 0.1413 | | 0.0600 |
| 3 | 0.1464 | | 0.0651 |
| 3 | 0.1439 | | 0.0626 |
| 4 | 0.1581 | | 0.0768 |
| 4 | 0.1631 | | 0.0818 |
| 4 | 0.1653 | | 0.0840 |

The results show that in the analysis of tan liquors over 98 per cent. of the total acidity may be obtained by this method (Tables I and II). The results in the presence of tannin are nevertheless too high, due to the reaction between the tannins and the carbonates and this error varies with the percentage of tannin. Since the liquors highest in tannin contain also the largest per cent. of acid, the error due to the breaking down of tannin is less important than it otherwise would be. It tends to make the results too high by a constant factor; that is, the increase is proportionately greater as the true value of the acid increases. The results, although inaccurate, bear the correct relation to each other.

As these results are concordant with those obtained with the gelatin method, no doubt this method also includes the acidity due to the tannins. Experiments showed that sodium hydroxide was used up in the same general proportion that carbon dioxide was liberated.

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In spite of the errors to which this method is undeniably subject, the following advantages can fairly be claimed:

There is no chance for the absorption of acid by bone-black, no loss of acid in the precipitate, no uncertainty of the end-point as in the quinine method, no tedious filtration of a gelatin precipitate.

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## NOTE ON THE DETERMINATION OF GLUCOSE IN LEATHER

*By F. P. Veitch*

In the determination of glucose in leather the provisional method of the A. L. C. A. directs that 400 cc. of the leather extract, which has been freed from tannin with lead acetate and excess of lead removed, be concentrated by boiling for two hours with the addition of 5 cc. of concentrated hydrochloric acid to a volume of about 90 cc., neutralized, filtered, made to a volume of 100 cc. and dextrose determined in an aliquot portion by the reduction of Allihn's Fehling solution. This procedure gives low results, as at this concentration a small quantity of dextrose is destroyed, amounting in some cases to as much as 5 milligrams. After much experimenting the following procedure was found to be rapid of execution and to give accurate results. An aliquot portion of the aqueous extract, representing from 2 $^1/_2$ to 5 grams of leather, is treated with 25 cc. of basic lead acetate solution, filtered, and excess of lead removed with anhydrous sodium carbonate or potassium sulphate. A portion of the solution equivalent to 2 to 4 grams of leather is boiled down with the addition of 5 cc. concentrated hydrochloric acid to a volume of 175 cc. to 190 cc., and the boiling continued for two hours under a reflex condenser, or in an open flask, keeping the volume of solution between 175 cc. and 190 cc. The liquid is then cooled, neutralized, transferred to a 200 cc. flask (filtered if necessary), made to volume, and an aliquot portion treated with Fehling solution in the usual way. The copper oxide must be thoroughly washed with hot water to insure the removal of alkali. If an aliquot portion of 100 cc. of the sugar solution be taken for reduction, thus making the volume of solution in which the reduction takes place 160 cc. instead of the prescribed 145 cc., the results in terms of dextrose are from .02 per cent. to .10 per cent. low.

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# REVIEWS

**The Determination of Moisture in Degras.** W. FAHRION. *Collegium*, 1908, pp. 21–2.—The author, who claims to have first published the crucible method cited by Alden (THIS JOURNAL, 1907, p. 12) from Procter's Laboratory Book, denies that drying with sand is more accurate, but is prone rather to give too high results, because of decomposition of the oil from the prolonged heating. With practice there is no difficulty in determining the end-point with the crucible method, especially if the novice first practice with dried sod oil to which a known weight of water has been added.

**Some Colloid Oxides as Tanning Agents.** DR. LÜPPO-CRAMER. *Zeit. f. Chem. u. Ind. d. Kolloide*, 1907, through *Collegium*, 1908, pp 24–6, 29–30. —The chemical reaction in the tanning of gelatine in the following cases is regarded as a hydrolysis of the metallic salts brought about by the gelatine. A coagulated gelatine film on a glass plate from a 10 per cent. solution made alkaline, on immersion in a silver nitrate bath becomes insoluble in boiling water; it is necessary, however, for the tanning of the gelatine that the silver salt be in excess. The tanning action of a colloidal solution of silver superoxide is still more marked; this solution is prepared by the action of ammonium persulphate on silver salts. The oxides of copper and mercury behave similarly, the product from mercuric salts being an extremely hard insoluble gelatine film. A discussion follows of the chemistry of silver albumen process of photography.

**Reply to J. Jedlicka's Criticism of the Official Method of Tannin Analysis.** H. R. PROCTER. *Collegium*, 1908, pp. 51–2.—The writer agrees with Jedlicka in the experimental results and assumes the responsibility for the inadequate prescription of chromium salt in the official formula, this being an oversight. He does not believe, however, that higher chroming is desirable and would prefer the general limits to be altered to 0.1–1.0 per cent. Higher chroming necessitates the use of more solution and prolongs the washing; it would also increase absorption of non-tans, giving results even higher than those of the filter-bell with chromed powder which have been shown to be too high. In washing, it is essential after squeezing the powder, to mix well with fresh water and allow to stand 5 minutes before second squeezing.

**The Colors Imparted to Leather by Vegetable Dyes.** JOHANNES PAESSLER, *Gerber Zeitung*, 1907, through *Collegium*, 1908, pp. 48–51.—Most natural dye-stuffs give leather a characteristic brown color of innumerable tones. In many cases these colors are affected by light, generally darkening. The effect most desired is a permanent light color, not only as a matter of fashion, but also as being best suited for further dyeing. In the *Versuchsanstalt für Leder Industrie* a series of experiments were made for comparison of the colors produced on leather by various tanning materials. The carefully tanned samples of grain splits were preserved in triplicate for 2 months, (1) in the dark, (2) in northern exposure to diffused daylight, (3) in full southern exposure. The colors were then measured by the Lovibond tintometer as first proposed by Procter and Parker (*J. S. C. I.*, 1895). The colors are analyzed as compounded of the three fundamental

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colors—red, yellow and blue—these three components being numerically rated. The numbers show the intensity and their ratios the color shades. A table of such colorimetric measurements is given for 21 samples. The results show essential differences; with the leathers not exposed to light, the lightest shades are furnished by gambier, sumac, sumac extract and algarobilla; the darkest and also reddest, by mangrove bark; the others are intermediate, in order from light to dark, myrabolams, valonia, oak-galls, quebracho extract (cold soluble), divi-divi, fir bark, quebracho extract (regular), mimosa bark, chestnut-wood extract, mallet bark, quebracho wood. Great differences in color also prevail; with sumac and gambier the primary tones are nearly equal, producing a neutral color, suitable for leather employed for bright dyes; with algarobilla, yellow preponderates; yellow to yellowish brown are given by divi-divi, oak bark, fir bark, mallet bark; light reddish to reddish brown by mimosa and quebracho extract and a decided red-brown by mangrove. The samples exposed to light showed an increased intensity in color, especially in the red tones. The light colors produced by sumac and gambier are changed the least. The shades produced by oak and fir barks deepen considerably without change of color. With mimosa bark, mallet bark and quebracho, the shade is not only deeper, but redder, a result not generally desirable. Quebracho extract shows less change than the wood itself. The author expects to extend this line of investigation to the results produced by the mixtures practically used.

**The New Method of Tannin Analysis.** *Ledermarkt.*, 1908.—The union of German Dye and Extract Manufacturers in an open letter declare the new official method to be less reliable than the old. Comparative analyses are quoted of duplicate samples sent out to various laboratories showing greater variations by the shake-method.

**Employment of Diastafor for Softening Hard Hides.** *Deutsch. Färb. Zt.*, through *Gerber-Ztg.*, 1908.—The hides are softened $^1/_2$ hour in a soap-bath to which some soda and tetrapol have been added. After thorough washing and rinsing, the hides are pressed and left over night (12 hours) in a solution of $^1/_2$ kilo diastafor in 30 liters distilled water. They are then pressed and the liquor preserved for re-use, requiring a renewal of half the quantity of diastafor. The hides are then dried slowly at a gentle heat. The sulphuring of white hides is safest after a diastafor treatment. After sulphuring, the hides should not again be placed in water. The sulphur odor is best removed by airing. During drying the hides must be well worked on the leather side with a hard tool. A subsequent washing with benzene is not permissible.

**Hop Tannin.** H. C. CHAPMAN. *J. Inst. Brewing*, 1907, 13, 646–652.—The tannin is precipitated by a saturated solution of cinchonine sulphate, filtered through asbestos mat in a Gooch crucible, and dried. Tests on pure gallotannic acid gave nearly theoretical results and were almost identical with those from similar tests on hop tannin.

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## PATENTS

**Method of Making Leather Tires. U. S. Patent No. 880,371** to R. J. ELLEDGE, Los Angeles, Cal.—A mechanical process of forming leather into the shape required for tires.

**Process for the Manufacture of a Leather Substitute:** PLUNDER and POLLOK. **French Patent, 380,941.**—Leather shavings are treated with an adhesive mixture prepared from the following materials: Oleic acid and colophony, equal parts, are melted together, and two parts of this mixture are added to a solution of one part casein, in five parts water. The whole mass is made into a paste, pressed into plates and dried.

**Russia Leather, and a Method of Manufacture Thereof:** J. W. and W. C. DUNN, London. **English Patent No. 13,475.**—After the hides are degreased and shaved to desired thickness, they are retanned in a suitable material and dyed. They are then placed between "crust" Russia hides to restore the "scent," and are finished in a similar manner to goat-skins for moroccos.

**Art of Converting Hides or Skins into Leather: U. S. Patent No. 881,246** to A. E. KELK, Louisville, Kentucky.—The hides or skins are subjected to a bath in a solution of nicotin, and the contact prolonged until the hair is loosened.

**Vacuum Pan: U. S. Patent No. 881,351** to A. P. SMITH, Phila., Pa.—An improved vacuum pan permitting of uniform distribution of the heating agent in the steam drums.

**Leather-Rolling Press: U. S. Patent No. 882,033** to C. VOSS, Neumunster, Germany.—An improved leather-rolling machine.

**Evaporator: U. S. Patent No. 882,043** to E. ZAREMBA, Chicago, Ill.—An evaporator having steam chests at opposite sides, connected by a group of horizontal tubes, so arranged as to improve the circulation of the liquid being evaporated.

**Process for the Extraction of Glue from Mineral-Dressed or Chrome-Tanned Leather: U. S. Patent No. 882,481** to A. R. WEISS, JR., Hilchenbach, Germany.—A process for extracting glue from mineral-dressed and chrome-tanned leather, consisting in treating the leather with hydroxide of the light metals and then boiling it with alkaline salts of the light metals at temperatures up to 125° C. till the glue is isolated.

**Process for Making Leather-Dressing from Sapped or Exhausted Tanning Liquors: U. S. Patent No. 882,489** to G. W. CHILDS, New York.—A process of treating sapped organic tanning liquors containing mineral acid impurities, by neutralizing or precipitating the mineral impurities, and then concentrating the purified liquors.

**Process of Making Liquid Leather-Dressing from Tanning Liquors: U. S. Patent No. 882,490** to G. W. CHILDS, New York.—A process consisting in mixing waste organic tanning liquors with active organic tanning liquors, and concentrating the mixture until it is of from 1.05 to 1.3 specific gravity.

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## THE TECHNICAL EXAMINATION OF TANNING MATERIALS AND LIQUORS.

*By Rowland A. Earp*

The present system of examining tanning materials or liquors is confined to the determination of the percentage of tan, of soluble non-tan, or insoluble matter, and of water, together with a measurement of the color. In addition to these determinations, in special cases there are also measurements made of the inorganic matter of the sample, and, in extracts, measurements of sulphites and adulterants. The present article has nothing to do with the matter of adulterants, except in a secondary sense.

The measurement of tannin may be said to have reached a fairly satisfactory standard of reliability and uniformity, for the

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attention that has been given to means for doing this has been very great. But although a reliable and uniform test of tanning materials as regards their tannin content is desirable, there are many other tanning properties of equal importance with their strength of tan, which it is equally desirable that attention should be given to, and which are equally capable of being expressed numerically in analytical reports.

Nor is the difficulty of determining these other factors insuperably great, and it seems a pity that years of valuable time should be occupied in researches which have for their object the decision of such questions as whether the shake or the filter-bell method is the better, or whether hide-powder should be chromed or not, or in which way it should be chromed. But when a convocation of chemists begins to gravely discuss the question as to whether a certain liquor is clear or not, and such similar minutiæ of procedure in chemical manipulation, the application of their energies to such hair-splitting problems leads one to think that the outlook on the part of the chemists is altogether too confined. But can it be true that the chemist looks no further than the mere determination of the percentage by weight of the tan ? If that is the whole extent of the outlook for chemists, then chemists are going to have a very poor time of it. After all, it is the tanner who makes the money and not the chemist, and if all the information which the chemist can supply to the tanner is the strength of tan in any sample, then the chemist must expect to have a very small share of the tanner's profits. And yet the only item of real value in an analysis of the present day is the percentage of tan and non-tan.

As one of the fraternity, and one who would prefer to live rather than to starve, the writer wishes to indicate that there are properties of materials and liquors other than the mere percentage of tan and of non-tan which, if expressed in reports, would give these a much higher value in the opinion of the tanner. He wishes also to make tanners realize this, so that they may ask from chemists much more information than they now do with regard to the comparative values and intrinsic qualities of materials and liquors.

Take, for instance, a new tanning material, the effects of

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which in the yard the tanner knows nothing about. The knowledge of the strength of the tan is of little help in judging how to use the material. The tanner has to find that out by expensive and hazardous trials in the tannery, which by means of a more complete laboratory report, would be rendered far less tentative and risky. It may be said that a new material does not make its appearance every day, and that the present materials are understood sufficiently well; but neither the former nor the latter arguments have much weight against the case for more efficient laboratory knowledge. The many brands of extracts, differing so much in qualities, and the expansion of botanical and forest surveys abroad are constantly increasing the number of tanning materials; and it is by no means certain that tanners are using the materials of decades, or even of centuries ago, with the greatest possible economy.

Before dealing with the tan-content, the writer will discuss the non-tan constituents of the sample. At present these are all given under one heading, but they should be differentiated into at least four. These are: (1) Gallic acid and its congeners; (2) acetic and other acids not contained in (1); (3) gums, starches, glucoses and resins, and (4) inorganic matter. The non-tannin matters of the first heading are perhaps the most important to the tanner. Although these bodies exist as non-tans in the material, they are valuable as the tans themselves, for they are almost completely used up in leather formation. The full substantiation of this statement is too long to enter into here, but the writer and a colleague are engaged in treating of this subject more fully, and hope to publish their work soon. Meanwhile, the fact that these matters are closely related to the tannins will suffice as evidence of the desirability of differentiating them from the rest of the non-tans. The chief practical benefit of their measurement is the light it throws upon the rationale and practice of the mixing of liquors.

The second component of the non-tans determines the initial acidity of the liquors apart from that capable of being produced by fermentation, or other secondary change, and apart from the tannins and gallic non-tannins. Such acidity also helps to determine the economy of the mixing of liquors besides being a useful guide in all circumstances where the acidity of the liquor plays a part.

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The third component is the base of all fermentative change. Besides indicating the liability of fermentation, it also gives the reserve of acid-producing power in the material. Most of the extraneous acidity of a liquor is due to change produced in the tannery through decomposition of this component of the non-tans, but some materials give a considerable initial acidity, and hence both (1) and (3) should be distinguished. The fourth component does not probably play an important part in the tannery; but even for this negative reason alone it should be considered separately, for at present it forms, in the analysis, a portion of the partly-active "soluble non-tan." It is sufficiently distinct from the others to deserve a place for itself.

The non-tans having been thus rapidly reviewed, the next important quality to consider, namely, that of diffusiveness, belongs both to the tan and to the non-tan, though it is with regard to the tan alone that it is of chief significance to the tanner. The diffusiveness of a tan is synonymous with its quickness of penetration, and is, consequently, one of the chief physical properties of a tan whereby the rapidity with which it will "strike through" is determined.

It is strange that more attention has not been given to this property of tans, for it is a property which is very readily measured relatively. There seems to have been little done in measuring the diffusiveness of the tans since the time of Graham, 40 years ago. Graham then measured the diffusivity of two tans— gambier and gallo-tannic acid— with the result that gambier gave a diffusivity of five times that of gallo-tannic acid. The great difference of the measurement in the two tannins, agreeing as it does with the relatively high penetrative action of gambier, shows the importance and significance of the property. Thus a most vital characteristic of tans, which a chemical test takes no cognisance of, might be thrust before the notice of the tanner, for attention would at once be arrested by a constant which, in two samples, differed as much as five times itself.

The application of the principle of diffusion to the analysis of tanning materials, and the thorough study of the subject, would not only be fruitful in giving the tanner the relative penetrating power of any material, but also help in distinguishing the different tans always associated together there.

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A second equally important property of tan is its rapidity of action. This, like the diffusion co-efficient, may be compared with a fixed standard, and so help in forming an idea of the general nature of the tan. This property is apt to get confused with the diffusivity, but it is a very different one. Diffusivity is a purely physical property of the tan, and is a measure of its rapidity of motion through any medium, hide-substance included. Rapidity of action, or of absorption, is a chemical property. For instance, a tan of great diffusivity but of small rapidity of action will quickly travel through hide-substance, but become slowly absorbed. Such is the characteristic of a "mellow" tan. The other extreme, a tan of slight diffusivity and intense absorption, constitutes an "astringent" tan —*i. e.*, a tan which would be liable to case-harden.

There are numerous grades of difference between these two extremes. The main point is to realize that diffusivity and rapidity of absorption are entirely distinct. As examples: Gambier has both properties in a high degree; new valonia has slight diffusivity with great rapidity of action; an old bark liquor has considerable diffusivity, but its rapidity of action is slight.

Not less important than these properties of tans are the two properties now to be considered. They do not appear to have hitherto had any general recognizance, and they require naming and explaining. The first may be called the "equilibrium-ratio" of the tan. It is characteristic which determines its tanning power at any one strength. For example, consider two small pieces of pelt, and let one be tanned in a large volume of a liquor of one tan, and let the other piece be tanned in a large volume of a liquor of another tan, the strengths of tan in the two liquors being supposed equal, and their volume so great that the tanning of the small piece of pelt makes no appreciable difference in their strength. When tanned, the pieces will, generally speaking, give different "weights," or different proportions of tan absorbed to the weight of pelts, notwithstanding that they were tanned in the same strength liquor. The equilibrium-ratio measures this difference.

As another illustration, consider two packs of hides of equal weight of hide-substance, and let one pack be tanned in a certain

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volume of liquor of a certain strength, and the other pack tanned in the same volume and same strength of liquor, but having a difference in this quality under consideration.

In this case the amount of the liquors is supposed to be limited, but sufficient to tan the hides through. In time the leather is tanned through, and will gain no more weight beyond that due to secondary causes. But the liquors will be found to be different in strength, one pack having absorbed more than the other. The "equilibrium-ratio" is measured by the ratio of the two numbers—(1) the percentage of tan in the liquor and (2) the percentage of tan in the tanned hide. For any one class of liquor at any one strength this ratio is constant, but it varies both for liquor of different qualities and also for the same liquor for different strengths. If this ratio were determined for all the known tans at certain strengths the values would be of incalculable value to the tanner. The value would enable him to judge the best stage at which to use the tans. The equilibrium-ratio varies between high limits. For liquors of 10° B. it may double or treble itself, so there is plenty of range to judge by.

The second of these two properties may be called the "efficiency" of the tan. To illustrate this, consider two hides tanned in different liquors, and consider the four quantities, namely, the gain in weight of the hides and the loss in strength (of both tan and non-tan) of the liquors. The ratio of the gain in weight of the hide to the loss of strength of the liquors in each case is the "efficiency" of the liquors.

Generally the efficiency of materials and liquors varies. It might be supposed that the two quantities are equal, and the ratio equal to unity, but they are not so. The efficiency may be either greater or less than uniting. So far as the writer has examined this property he has got an extreme difference of about 30 per cent. Thus, 3 lbs. of tan of one variety may go as far as 4 lbs. of tan of another variety. The explanation of the difference is to be found in the varying amount of water which either enters into union with the tan in the act of formation of leather or else is held by the leather in a manner similar to the water of crystallization of salts.

The very practical nature of this property of tans is obvious.

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It may be easily measured, and measured far more quickly than could be done by a practical trial in the tannery, and far more accurately.

Nor is there any difficulty about determining the equilibrium ratio, and the writer considers that the study of these properties of tans will well repay the chemist, for they all represent qualities of the tans which are of vital importance in governing the management of the tan-yard. However, it is necessary that tanners should thoroughly understand the full significance of these properties in order to be able to make use of them, and for this reason the writer first places them before the tanners rather than before the chemists; for if tanners find they will be of value then the chemist will take care that they are supplied. —Leather Trades Review.

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## NOTE ON THE PHELAN-FISKE ACID METHOD.

*By W. H. Teas*

Although the writer has not had the opportunity of testing the acid method described by Messrs Phelan and Fiske in the last issue of the *Journal,* some of the published results of experiments by the authors, and the erroneous assumption as to the relation of tannin to acid content, would indicate that the proposed method is not one that will stand the test of practical usage. The influence of the tannin present on the carbonate is too great to allow its effect on the result without a correction, and even if this correction could be made with any degree of accuracy, the corrected result would not be sufficiently absolute to inspire confidence.

The statement that the tan liquors highest in tannin contain the highest amounts of acid, is not correct, as the acid content of a liquor is determined by the nature and age of the liquor, the local method of handling the liquors and the position of the liquor in the system of tanning in use.

Concordance of a proposed method with an unsatisfactory method in use, is not a recommendation, particularly when a source of error in the proposed method is apparent.

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## MARCH MEETING OF THE BRITISH SECTION OF THE I. A. L. T. C.

A meeting of the British Section of the I. A. L. T. C. was held on Saturday, March 21st, at the University of Leeds. Professor Procter presided.

A paper was read by J. G. Parker and A. T. Hough on "The Standardization of Hide-Powder," in which they advocated that the next Conference of the I. A. L. T. C. should fix narrower limits for the degree of acidity in hide-powder. A number of results were communicated, which they had obtained by bringing various hide-powders to a definite degree of acidity. The authors suggested that those hide-powders which did not fulfil the conditions laid down by the I. A. L. T. C. for acidity should be standardized by the addition of the necessary amount of caustic soda previous to chroming. The acidity of the hide-powder having been first ascertained by Bennett's method, a sufficient amount of hide-powder to correspond to 6.5 grams of dry material is weighed out, and 10 times its weight in water added; a sufficient amount of N/10 caustic soda is then run in to bring the acidity to the desired degree, and the mixture is rotated for 15 minutes. The powder is then chromed in the usual manner with the standard solution of basic chromic chloride. After the usual washing and pressing the analysis is carried on in the ordinary way.

After some discussion, Mr. Bennett proposed that this meeting of the British Section agree "that the method of adjusting the acidity of the powder immediately prior to analysis was within the rules of the I. A. L. T. C." This was seconded by Wood, and carried. The authors promised to publish the work in the *Collegium* as soon as possible.

Professor Procter then made a general statement with regard to the present method of analysis. He agreed that the change from the old filter method to the present official shake method had undoubtedly caused considerable trouble in the leather trade as all changes were bound to do, but he was convinced that both tanners and extract manufacturers were now realizing that the present method of analysis was more truthful, and gave to both tanners and extract manufacturers a more reliable and accurate

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return of the amount of available tanning substance contained in the material analyzed.

He then reviewed the work which had been done on the subject both by outside workers and by the International Commission, and explained why no ratio between the two methods could be fixed for all extracts. He pointed out that sulphited extracted must come under a separate category, as they were not comparable with other extracts, because the presence of bisulphites acted in a peculiar manner, in some cases causing a greater absorption, and in others a lesser absorption, dependent upon the condition of the salt contained in the extract. He further pointed out that extracts extracted from the wood under pressure, or by the addition of alkaline salts of sulphurous acid, contained a high proportion of substances not absorbed by hide, and which were of no value to the tanner. Such extracts were bound to suffer very materially by the new method of analysis, but extracts manufactured at ordinary pressure and temperature did not show such a large variation when analyzed by both methods. He illustrated this by figures obtained in his own laboratory during the past few weeks.

Professor Procter then invited the gentlemen representing the extract trade to bring forward any matter they desired discussed.

Mr. Classen (Messrs. Blackley, Young and Co.) brought forward a number of results of analysis of the same samples of extract by various chemists, showing varying differences between analysis by the old method and the new; he said that he did not think that the concordance between chemists was as close as with the old method, and considered that it was necessary for chemists to have more practice with the new method before greater agreement could be obtained. On behalf of the extract trade he begged the chemists present to do all in their power to find out the causes of difference.

Mr. Classen was followed by Mr. Rink ,who also gave a number of figures representing analyses done by various trade chemists in October and November of last year. These results did not show satisfactory concordance, but from more recent analyses done in February the agreement was much more close, and he expressed himself as being more satisfied than he had been

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at the commencement. He trusted that the matter would be taken up seriously by the chemists, and that even closer agreement would still be obtained. Mr. Rink also drew attention to the fact that the French and German extract manufacturers still adhered in many cases to the old method, and this was causing further confusion. In this country, when receiving a foreign analysis, they did not know where they were, as some extract manufacturers had their samples analyzed by the old official method, and others by Paessler's chromed hide-powder, which, although illegal, was still being used by some manufacturers because it showed an unduly high percentage of tanning matters. He thought that surely all members of the International Association of Leather Trades' Chemists should work by one method, and one only.

Mr. Clements (Yorkshire Dyeware and Chemical Company) illustrated a serious case of differences obtained on a sample of their extract by three chemists, which showed variations of over 2½ per cent. His firm had had to pay a claim to tanners on this delivery, and it had subsequently been proved that the delivery was up to the guarantee.

Mr. Appleton and Mr. C. E. Parker spoke on behalf of the tanners, the latter pointing out that he had found the results by the new method approached far more closely the results obtained in the tannery than the old method. He considered that the change was a step in the right direction, and he trusted that as the details of manipulation became more defined, that the method would yet develop into a most valuable one. Even in its present condition he considered it better than the old method, which gave too high results in tanning by returning many of the non-tanning substances as tanning matters.

Professor Proctor thanked the gentlemen for their candid criticism and for attending the meeting, and assured them, on behalf of the chemists, that everything would be done to bring greater uniformity into the work. He emphasized the fact that non-tannins did not unite to make leather, but consisted largely of glucose and substances of a similar nature which were always present in all tanning materials, and that it was cheaper, if non-tannins were required in the tan-yard, to add them to the pits for the sake of development of acid. He also pointed out that some

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of the non-tannins consisted of decomposition products of cellulose, which had no affinity for leather.

Dr. Parker stated that he had for several years made a practice where he was in disagreement with any chemist, of always being willing to submit his sample to a referee, and that if proved wrong he paid the referee's fee, and made no charge for his own analysis when it was proved to be inaccurate. Professor Proctor stated that he was also willing to do this, and Messrs. Turnbull and O'Brien also agreed. Mr. Charles Parker pointed out what a great benefit to both tanners and extract sellers this would be if it became a universal custom among public chemists analyzing for the leather trade. The details of fixing a limit of error was left to the chemists.

In the afternoon session Dr. Nierenstein read a short paper on the "Constitution of Tannin," giving his views on the constitutional formula of some of the products.

The members of the British Section then discussed further questions with regard to the supply of hide-powder, and it was agreed that all hide-powder should be drawn from one source, and, as far as possible, from one large delivery. It was pointed out that the American hide-powder used by the American leather trades' chemists was more easy of manipulation than Paessler's powder; it had less soluble matter, and was more easily squeezed, and was held by some members to give more concordant results. Professor Procter said that he had sent to Dr. Paessler a sample of the American powder. Dr. Paessler had answered saying that he would endeavor to improve his powder, so that the difficulties of squeezing and washing could be minimized.

After discussing various other matters the meeting terminated with a vote of thanks to the chairman.

## THE DETERIORATION OF MODERN DYED LEATHERS.

At the last meeting of the London Section of the Society of Dyers and Colorists, a paper was read by F. J. Farrell on the "Germicidal Powder of Petroleum Benzine." In this contribution he briefly outlined the process employed in dry cleaning articles by immersion in benzine, having a specific gravity of 0.740 to 0.780, or lower. The articles were immersed with the benzine in a rotating machine, the spirit dissolving out the

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grease which held the dirt, and which was removed mechanically by rinsing. After giving definitions of what were really antiseptics and disinfectants, the author proceeded to describe the experiments he had followed out on properly prepared silk fibers with a view to investigating the claims of benzine as a germicide. The results of the experiments showed that benzine and benzol, acting for as long as six hours and a half, did not possess any germicidal power, and that they did not appear to act as antiseptics, as immersion in these liquids for that time did not appear to affect the growth of the organisms tested. Carbon tetrachloride, however—which, by the way, has been suggested as a degreasing agent for leather—acted as a germicide, the bacillus being killed in all cases.

A lengthy paper was then read by Mr. M. C. Lamb, of Herold's Institute, on the "Deterioration of Modern Dyed Leathers." In this the author drew renewed attention to the bad state of many of the modern bindings, and to the valuable data collected on the subject by the committee appointed by the Society of Arts. Mr. Lamb dealt at length with the various causes which caused the decay in modern leathers, but the major part of the paper was devoted to a consideration of a series of valuable experiments which he had carried out with a view to testing the actual effect of gas fumes on several tannages and varieties of leather. Bark, sumac and many other vegetable tanned leathers, chrome and alum, had all been subjected to a prolonged series of tests in a small room fitted with a gas burner, and the condition of the specimens carefully noted at certain stated intervals. In all cases the vegetable tanned leathers were severely affected, most of them being quite disintegrated and useless. A few, however, seemed to have been protected to some extent by special grain finishes, but in the case of chrome and alum leathers it was clearly proved that they were able to resist the deteriorating action of the products of combustion in an infinitely superior degree to the vegetable leather. Many of the chrome dyed and finished leathers were scarcely affected, and the result of Mr. Lamb's experiments seemed to prove that for certain varieties of book-binding, the use of this material is strongly to be recommended, especially where hard wear and lasting properties are of first consideration.

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A good deal of interest was also taken in specimens of leathers which had, through the kindness of Mr. F. Y. Golding, headmaster of the Leather Trades' School, Bethnal Green Road, E., been sent Mr. Lamb for inspection. These were cut from whole skins, which had been hung on the school walls for a few years, and embraced practically all the shoe leathers in vogue about eight or 10 years ago. Without exception all the vegetable material was perfectly rotten, even the heavily curried wax calf being absolutely useless. A specimen of alum tanned calf, however, had stood the exposure very well indeed, and was practically unaffected.

At the conclusion of the paper a lengthy discussion ensued, Mr. Lamb replying to several points raised by members, and being heartily thanked for his valuable paper.

## THE THEORY OF TANNING[1].

Mr. Ferdinand K. Kopecky, in *Collegium*, Nos. 268 and 269, gives an article on "The Science of Leather Manufacture." The article is purely theoretical, and a good many scientific terms are used, but it is none the less worthy of notice. The theory of tanning, although so incomplete is always interesting, and notwithstanding that the manufacture has not so far derived much benefit from attempting to work upon scientific lines, there is no reason that it should not do so in the future, when the theory of the process is better understood. Mr. Kopecky's article gives one an excuse for writing upon a subject which hitherto has not had much of a practical bearing, and both his special ideas and also ideas of a more general nature will be discussed in brief.

It is first of all necessary to define a few scientific terms in order to make this article intelligible to the general reader.

### *Some Definitions.*

"Chemical" and "physical" are qualifying terms referring to changes occurring in material substances. In order to obtain a complete idea of their respective meanings a very full knowledge of natural science is required, though such a deep insight is not necessary here. It is sufficient to state that a chemical change concerns the nature of the inner minute structure of

[1] A discussion appearing in *The Leather Trades Review*.

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matter, whereas physical change concerns the body as a whole. "Diffusion" is that natural physical process, which when a body is dissolved in a liquid, tends to dispense it equally through the whole volume of the liquid. Diffusion of a substance in a liquid continues until it is perfectly evenly distributed. It is a very powerful force, and may be utilized to do work. For instance, if a soluble substance be placed at the bottom of a vessel filled with water, the force of diffusion will in time, without any stirring, lift the dissolved substance to the top of the liquid until the concentration of the top layer is equal to that of the bottom. Diffusion is a physical process, because the substance diffused is not changed in nature. It is only changed in position and concentration.

"Dissociation" is a chemical process which occurs when some substances are dissolved in water. For instance, aluminium sulphate is a single substance formed from alumina and sulphuric acid, but when this is dissolved in water it is partly broken up into its original constituents, and the solution contains free sulphuric acid and free aluminium hydrate, both being perfectly evenly distributed all through the solution by the process of diffusion. Dissociation is a chemical process, because each minute particle of the matter dissociated is broken up into two or more particles. "Dialysis" is a phenomenon very frequently occurring in nature, and especially in organic life. It is a separation of two or more substances occurring mixed together in a solution, by means of the process of diffusion, and made possible by the fact that each individual substance has a diffusing speed of its own. Just as in running a race, the competitors separate according to the speed with which they travel, so do the dissolved substances separate according to the speed with which they diffuse into the less concentrated solvent. As an example of dialysis, we may take the process of making dialyzed iron, a very important medicinal preparation. To make this preparation, a strong solution of chloride of iron (a compound of iron and hydrochloric acid) is placed in a "dialyzer," which latter floats over water. The dialyzer is a shallow vessel, having a bottom made of parchment. The parchment allows diffusion to take place through it, but prevents any mechanical mixing of the solution in the dialyzer with the water below. The chloride of

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iron dissociates into hydrochloric acid and iron hydrate. Hydrochloric acid is very diffusible, and quickly passes through the parchment into the water below. Iron hydrate is only a slow diffuser, so chiefly remains behind, and is ultimately left in the dialyzer practically free from hydrochloric acid. Dialysis is a physical process, for only separation of two substances (in the example quoted already broken apart by the chemical process of dissociation) is involved.

*Crystalloid and Colloid.*

"Crystalloid" and "colloid" are two terms denoting substances, which are respectively very quick and very slow diffusers. Besides having these two extremes of diffusive ability they have other properties associated with them. Crystalloids are crystalline, or can be rendered so. Colloids are gelatinous or gummy, and cannot be crystallized. It is important to realize that one and the same substance may exist in either form. For instance, iron hydrate, as prepared by dialysis, is a colloid; but iron hydrate may also be prepared in a crystalline condition. Similarly aluminium hydrate and chromium hydrate can exist in the two forms.

Of the two forms the colloid is the unstable non-permanent one, and either time or some slight upsetting influence such as drying or slight warming may be sufficient to bring about a change of state to the crystalloidal condition. Crystalloids are quite stable, and can only be brought back to the colloidal condition by special chemical or mechanical means. All inorganic colloids have also a crystalloidal form into which they readily transform, but there are many organic colloids which do not appear to have a crystalloidal counterpart. Yet many organic colloidal substances experience certain changes into more stable and permanent conditions, which, like the transformation of hide-substance into leather, are probably merely changes of physical state from the colloidal to a crystalloidal or semi-crystalloidal condition, and which are strictly analogous to the change which inorganic colloids undergo. This reasoning is supported by the fact that where, in inorganic chemistry, there exist two forms—colloidal and crystalloidal—of the same substance, the colloidal form is always soluble, and the crystalloidal form insoluble. The same difference of solubility is found to occur when organic colloidal soluble substances experience these changes, the substance resulting from the change being insoluble.

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*Theory of Distribution between Liquor and Hide.*

These are all the terms that it is necessary to describe, though some explanation is required of the relationship of the solvent action of two distinct and contiguous solvents to the substance dissolved. For example, alcohol dissolves in water and also in oil. If oil be added to a solution of alcohol in water, there is no apparent mixing of the two solutions, and the oil floats on the top, or, at any rate, remains separated, but in reality part of the alcohol leaves the water and goes into the oil. Again, if oil containing alcohol be added to pure water, the alcohol will partly leave the oil and go into the water. In all cases where there are two solvents in touch with one another, and a soluble substance is dissolved in them, the substance dissolved will distribute itself between the two solvents according to a fixed law depending upon the nature of the solvents and of the substance dissolved, and also depending upon the concentration of the substance dissolved, and upon the temperature. It is supposed that there is no chemical action between the three substances, and no physical change excepting that proceeding from diffusion, which enables the distribution to take place. When chemical action comes into play, or when other physical changes occur, the relationship is much more complex.

It is necessary to consider two solvents in order to probe the theory of tanning, because in tanning two solvents are involved; (1) the solution of tan, and (2) the colloidal hide substance, which also acts as a solvent.

If, in tanning, there was no process involved beyond solution and diffusion and consequent distribution of the tan between the two solvents, tanning, and the theory of tanning, would be a very simple matter. As it is, there is a physical change occurring in the hide-substance. There may be a chemical change as well, and this brings us to the article under discussion, for Mr. Kopecky says there is no chemical change.

*Tannage with no Tan—The Auto Process.*

The most simple tanning process is that where no tan is used. A hide may be tanned by simply drying it. Even quite supple leather may be thus made if the hide be kept in motion while the process of drying is going on. The tanning action is quite apart from any fatty matters within the hide, for a perfectly de-fatted

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hide will tan thus. Leather thus made is not very resistant to the action of water, or of decomposing agents, but it is much more so than the original wet pelt. In this case what action goes on is brought about by the process of drying. The action is also permanent to a great extent, for on wetting back leather so made it never quite returns to its original condition, and tanners know well that dried hides always tan differently, and make a different class of leather from that made from the same hides, but not previously dried.

The tanning of hide by drying it may therefore be regarded as a physical change in the direction of the crystalloid state, though it must be remembered that the crystalloid state is never quite reached. It may be so that on drying, and wetting back, and drying again, a more completely tanned product may be obtained; and the satisfactory nature of the footwear of some savage tribes who draw the fresh hide over their feet may be due to the repeated alternation of wetting and drying incurred during exposure to the weather.

*Formaldehyde Process.*

The next process of tanning in order of simplicity is formaldehyde tannage. It may be considered similar to the former, except that the physical change in the hide from colloid to crystalloid is conducted to a much greater extent. It is impossible to consider it as a chemical process (unless it is classed under the category of "catalytic processes," for particulars of which readers must look up works on chemistry), for the amount of formaldehyde required to produce the leather is so minute as to make it impossible for the composition of the leather to be anything else than pure hide-substance. The formaldehyde acts more probably as an accelerator towards the change which produces the less colloidal and more permanent and stable leather substance.

The two tannages just mentioned are interesting, for they show that hide-substance itself contains all that is necessary for the production of leather apart from any external tanning agent. Consequently, before attempts are made to theorize upon tanning processes proper, the cause of the change into leather in these two processes has to be accounted for. Kopecky does not touch upon the auto-process, and the formaldehyde tannage he con-

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siders as a kind of oil tannage. Procter considers the auto-process as a kind of oil tannage also, the oil involved being supposed present naturally in the hide. This view is quite untenable, since, as already remarked, hide-substance absolutely freed from fatty matters will tan similarly. The only possible cause of the change into leather is, therefore, a change in the hide-substance itself; probably simply a physical change of state in the direction of the crystalloidal condition.

*Mineral Tannages.*

Of the mineral tannages, any one may be selected as an example. Alum tannage is, perhaps, the best known, so will be considered, though what will be said refers to all mineral tannages. When a hide is placed in an alum solution both the acid half of the dissociated alum salt, and also the aluminium hydrate half diffuse into the hide substance. Whether the hide has a great attraction for the aluminium hydrate, or whatever may be the cause, the fact remains that it is chiefly the hydrate which enter the hide, and what is contained of the original alum within the hide when diffusion is finished is the same as that retained within a dialyzer when the alum salt is dialyzed, *i. e.*, colloidal aluminium hydrate.

Thus the hide has some sort of attraction for the colloidal hydrate. It appears that the reason of the attraction is that the portion of the alum salt attracted is both colloidal, and a hydrate; for it is well known that all mineral salts, which can be separated by dialysis into a colloidal hydrate and into the acid, are tanning agents, and it is always the colloidal hydrate portion which is absorbed. Hence the nature of the metal from which the salt is formed is of secondary importance. The reason for the absorption of the colloid may be that this latter, being an unstable physical form of the hydrate, the two substances, namely, the hide substance and the colloidal hydrate, require one another to facilitate a mutual transformation into a more stable condition. If this is the case, then, Mr. Kopecky's opinion that everything may be explained upon physical reasoning may be correct. But the fact that all the mineral tanning agents, besides being colloids, are hydrates, and also that Procter has done work which tends to show that hydrates form chemical

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compounds with hide-substance, makes possible a chemical reason for the absorption of the colloidal hydrate.

What happens when the hide-substance is removed from the alum solution and finished and dried is mainly physical in nature. The alumed hide may be washed in water without losing much of the alum contained in it whilst being freed from the acid portion; for the latter, as explained already, diffuses out very quickly, whereas the former is more fixed. On drying, the associated alum hydrate and hide-substance become converted into the insoluble, stable condition of leather—merely a physical change as in the case of tanning without tan, but more complete, because aluminium hydrate completely changes into the non-colloidal form on drying, and, perhaps, also because the asosciated alum causes the hide-substance itself to become more completely converted. Mr. Kopecky considers that alum-tanned leather is so permanent and resistant against the action of water, because each individual fiber is coated with a film of non-colloidal alumina which protects the hide-substance within it. It seems more reasonable to suppose that the alum is evenly distributed through the whole substance of the fiber, and that this intimate mixture is itself endowed with the resistant properties of alum-tanned leather.

### *Vegetable Tannages.*

Mineral tannages are complicated enough; but they are very simple when compared with the intricacies of vegetable tannages. Vegetable tannin is colloidal, like the mineral tannins. It has certain chemical characteristics also in common with the mineral tannins; but these are too technical in nature to be discussed here. It seems likely, however, that both a colloidal nature and also this peculiar chemical nature is necessary to a vegetable tannin, just as they are associated together in the mineral tannins. As a partial proof of this reasoning it may be stated that certain vegetable crystalloidal non-tans, when associated with vegetable colloidal non-tan, make a mixture which will tan, which neither by themselves will do. For instance, gallic acid is a crystalloid and a non-tan, and gum is a non-tan, but a colloid; yet a mixture of gallic acid and gum will tan. What is so difficult to give a reason for is the extraordinary absorptive power of hide-substance for tan, and although Mr.

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Kopecky does not think so, it seems most likely that there is a chemical attraction between the hide-substance and the tan, of a nature not very different from that which has been just now suggested in the case of mineral tannages. The subsequent behavior of the tan absorbed by the hide is similar in some respects to mineral tan. Once the tan is in it will not readily come out again, both on account of its colloidal non-diffusive nature and also on account of the retaining power of the hide. Also on drying the leather, the tan becomes more fixed, as is the case with mineral tanned leather. But there are many changes occurring within vegetable-tanned leather during the process of tanning which have not their counterpart in mineral tannages, and which depend to a great extent upon the nature of the tan used and the means of using it. It is the nature of these subsequent changes upon which to a great extent the qualities of the leather depend. They can only be just named in this article.

*Combination Tannages.*

Mr. Kopecky considers that combination tannages are a practical impossibility, though his reason for so doing is not clear. The vegetable tanning of a hide which has been previously tanned with alum or chrome and allowed to dry may not be satisfactory; for once a mineral-tanned leather is dried it can never swell properly again sufficient for the purpose of vegetable tanning. Even a mineral-tanned leather that has not been dried, but has been tanned some time, may not tan satisfactorily with vegetable tan, for mineral-tanned leather even on keeping in the wet experiences a partial change towards the stable non-colloidal form. It is essential for tanning with vegetable tans that the hide should be in a soft colloidal condition, and perhaps where combination tannages have failed, the preliminary mineral tan has been allowed to convert the hide-substance to a too great extent either through too great a concentration of the mineral tan, or through too long a delay in applying the vegetable tan.

*Oil Tannages.*

Lastly, oil tannages have to be considered. Mr. Kopecky, classes these also as physical in nature. Of course, it does not matter a bit whether tannages are physical or not, from a prac-

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tical point of view; but this article, with many apologies from the writer, is intended to be chiefly theoretical. Mr. Kopecky considers oil-tanned leather to consist of ordinary fibrous hide-substance having a coating of a fine film of oil all over the fibers, the oil-film ensuring stability and resistance, and giving the characteristics of leather to the hide. He considers the change in chemical nature (which is known to occur) of the oil used as of secondary importance. It seems preferable to consider the oil as distributed right through the substance of each fiber, and the leather itself as physically changed hide-substance, the change having been brought about by association with the oil, something similar to the action in formaldehyde tannage. The large amount of oil used, and the chemical change which this undergoes, makes possible a chemical change also of the hide-substance.

The final conclusion upon reviewing the different tannages is that physical changes, though not the only kind involved, are the most important, chemical changes taking place, especially in oil tannages, and especially in vegetable tannages subsequent to the absorption of the tan. The chief physical change is of the nature of a colloidal to a crystalloidal condition, brought about (1) by drying; (2) by the association of small traces of substances which accelerate the change; (3) by the association of a second colloid, the change of state also taking place in the added colloid—(Anonymous).

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DEAR SIR,—In *Der Gerber*, No. 802, p. 33, under the heading of "A New Theory of Tanning," Professor Stiasny criticises the above article on the theory of tanning.

His article is mainly directed towards the sub-section of mine where I briefly define the nature of crystalloids and colloids. In particular it is directed towards my statement that the same substance can exist both in the crystalloidal and in the colloidal form. This statement Professor Stiasny says is wrong, and consequently my treatment of the theory of tanning is wrong, since it is based upon wrong conceptions. I quote my original statement:—

"It is important to realize that one and the same substance

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may exist in either form. . . . All inorganic colloids have also a crystalloidal form into which they readily transform, but there are many organic colloids which do not appear to have a crystalloidal counterpart. Yet many organic colloidal substances experience certain changes into more stable and permanent conditions, which, like the transformation of hide-substance into leather, are probably merely changes of physical state from the colloidal to a crystalloidal or semi-crystalloidal condition, and which are strictly analogous to the changes which inorganic colloids undergo."

I wish in this letter to first show that colloids do exist in a crystalloidal form.

Colloidal Aluminium Hydrate: The ordinary gelatinous precipitate is found in nature as gibbsite, a fibrous translucent mineral. Hydrargyllite, a mineral occurring in regular six-sided prisms, is also a hydrate of alumina.

Colloidal Iron Hydrate: Hydrated oxide of iron occurs abundantly in nature crystallized as göthite, or needle iron ore.

Colloidal Chrome Hydrate: This rarely appears by itself in a crystallized condition, but in conjunction with the iron hydrate it occurs crystallized as chromite.

Colloidal Silicic Acid: Crystallized hydrated silicic acid, and crystallized hydrated silicates of aluminium, chrome and iron occur abundantly in nature, and, indeed, form the greater part of the earth's crust.

That all these minerals have passed through colloidal stages before reaching their final stable insoluble crystalloidal condition any geologist will admit.

As I stated in the article, organic colloids do not always appear to have a crystalloidal counterpart, but there are some which do. Tannin may be obtained in an insoluble crystalloidal condition. There are many organic colloids which have a semi-crystalloidal state, as, for example, leather, casein, starch and cellulose.

So much then in defence of my statement that substances can exist in both insoluble crystalloidal, and in colloidal states.

Professor Stiasny only distinguishes two states: one, the hydrogel, is insoluble and gelatinous; the other, the hydrosol,

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is soluble and viscid or gummy. These two states are interchangeable and differ only in hydration and agglomeration. But they do not cover the range of changes to which colloidal substances are subject to; changes which, like the change from hydrosol to hydrogel, are only concerned with the hydration and state of agglomeration of molecules. I distinguish three other degrees of change as follows:—

| | Degrees of Colloidal States | Examples |
|---|---|---|
| 1. | Insoluble crystalloid .... | Crystallized alum, hydrate crystallized insoluble tannin. |
| 2. | Insoluble semi-crystalloid | Leather, starch, cellulose. |
| 3. | Insoluble hydrogel ..... | Gelatine some tannins. Gelatinized starch, hide substance. |
| 4. | Soluble hydrosol..... | Soluble gelatine. Most tannins. |
| 5. | Hyper-colloid..... | Gallic acid, pyrogallol. Leucine. |

The inorganic colloids range from one extreme to the other. One instance is sufficient, that of aluminium hydrate. I have already shown that aluminium hydrate exists in the insoluble crystalloidal state. This hydrate may also be so changed that it loses all properties of a colloid, and becomes soluble and diffusible—two crucial properties of an ordinary soluble crystalline substance. This state I have termed the hyper-colloidal state. It is probable that under suitable conditions any one colloid, whether organic or inorganic, can be got into any of the five states.

I think it is fairly obvious that the hydrogel and the hydrosol states are insufficient to measure colloidal changes thereby. Take leather for example. It is not a hydrogel, nor yet a hydrosol. Does it then cease to be a colloid? I do not think it does, and have assigned it a place in the scale of colloidal states between the insoluble crystalloid and the hydrogel. I am not sure that under certain conditions leather may not be obtained in an insoluble fibrous crystalline mass something similar to asbestos, thus taking its place at the head of the table.

It is also plain that the process of tanning raises both constituents, hide and tan, in the table; or, as I stated in my article, the process of tanning is a change of physical state towards the insoluble crystalloidal condition. For instance, limed hide belongs to No. 3 in the table, and tannin belongs to 3, 4 and 5.

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Leather belongs to No. 2, both constituents being changed towards the crystalloidal state. Also, the nearer hide-substance approaches the insoluble crystalloidal state the less tan will it combine with (Earp: *Collegium*, 281, p. 379). This result I was not acquainted with when I wrote the articles, and came as a welcome surprise to me. It proves almost without doubt than tanning is chiefly a change of colloidal state.

I am, dear Sir,

Yours truly,

THE WRITER OF THE ARTICLE.

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DEAR SIR,—The popularization of science some of the greatest scientists, especially in this country, have considered as a task worth their attention, and it is universally acknowledged, how great an advantage this his always been for the public as well as for science itself. Just as great, however, is the damage done, when people enter this work, who themselves have no clear ideas about the principles of the special part of science to be dealt with, and allow themselves to be led astray by vague analogies to obviously wrong and even positively false statements.

These remarks refer to an article entitled "The Theory of Tanning," and to the reply of the anonymous author to a criticism by Professor Stiasny in the *Gerber* (No 802, p. 33), which reply precedes this article. I do not think it worth while to go through the whole of these articles and to show all the slighter mistakes. It will be sufficient, I hope, to prove simply:—

1. That the anonymous writer has no clear ideas of the things he talks about;

2. That his new theory of tanning is obviously wrong and moreover unnecessary;

3. To show the mistakes, which led him to his wrong conclusions;

4. To show the positively false statements in his articles.

Ad. 1. In the very beginning of the first article the anonymous author gives the definition of what is a crystalloid and a colloid, as it was first given by Graham, and as it is found in every text-book of physics or chemistry, namely, that crystalloid is a compound of greater, colloid one of small, diffusive power. Later on, however, he gives as his theory of the tan-

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ning process that the transformation of hide into leather is brought about by a change from the colloidal towards the crystalloidal state. Let us bring that to the logical form:—

(*a*) Crystalloid diffuses quicker than colloid.

(*b*) Neither hide nor leather diffuses at all.

(*c*) Therefore the formation of leather from hide is brought about by a change from colloidal towards crystalloidal state.

I hope that this sample of logical thinking would be enough to prove my first point. But, besides, the writer constantly talks about "insoluble crystalloids." If they are insoluble, let me ask him, how does he know anything about their diffusive power? And if he does not know, how can he call them crystalloids? Possibly because they form crystals?

One more instance. In the last article he corners us, so to speak, with the question: As leather is neither a hydrosol, nor a hydrogel, though it does not cease to be a colloid, is it not clear that there must be states of colloids besides these two? But the two walls forming this corner are very thin, and we easily shall break through. First, I do not see a reason why we should not consider leather in water as a gel as well as hide, at least, some leathers, for instance, an ordinary vegetable tanned one. It absorbs water on soaking and swells with it, though not so much as gelatine or hide does; it loses it on drying, and takes it again on resoaking; that it does no longer dissolve on boiling, this property it shares with alumina-hydrate, the author's favorite example. And as for the leathers, which are not influenced by water, as chrome leather or vegetable tanned leather after drying at high temperatures, in fact, not any more influenced than some asbestos-fiber thrown into water; will he still consider these as colloids? He himself seems to answer in the negative, as he says that—"Alumina-hydrate completely changes into the non-colloidal form on drying." I cannot find a difference in the behavior of perfectly dried chrome leather and this alumina-hydrate towards water.

Just let me say one word more about the class of compounds the anonymous writer terms hypercolloids. As long as he upholds his definition of colloids and crystalloids, there is no room left for such a new class; either the compound in solution shows a rate of diffusion comparable to common salt or sulphuric acid;

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then it is a crystalloid; or it does not, then it is a colloid. Now, as for instance gallic acid in water, according to Peternò, shows the molecular weight of about 1,800, this is comparable to that of the undoubted colloid wolframic acid, whose molecular weight is about 1,700. But as the diffusive power not only depends from the molecular weight, but also from the form of the molecule, a spherical one, for instance, not having to overcome the same resistance on moving in the medium as a cubical one, it is evident that a body, though of rather high molecular weight, may have a considerable diffusive power. The statement finally that alumina-hydrate may be obtained "in diffusible form," of course, is very interesting indeed, only a little more than a simple statement will be necessary to make us believe it, if it is supposed to mean anything else than the extremely slow diffusion noticed in every hydrosol.

So much, then, for the first point. As to the second, that leather is, in the opinion of the anonymous writer, formed by a change of the hide from the unstable colloidal towards a stable crystalloidal form, tanning agents working as accelerators of the reaction, the experience of physical research shows that if you have two modifications of the same compound, one stable, the other unstable, in a condition where the transformation of the latter into the first has just begun, and you keep them in the same condition, the reaction will never stop before the whole of the body is converted into the stable form (cf. Nernst, *Theor. Chem.*, p. 584). Now, take a simple case. Chrome leather is formed by bringing hide in contact with basic chromium-salt solutions. Will the writer really make us believe that on keeping up this condition we shall ultimately get his "fibrous mass something similar to asbestos"? That is why this new theory is wrong; but, as I said, it is unnecessary as well. For, if from two compounds we get a combination, nobody will be astonished to find properties of both of them changed. That is quite clear in the case of chemical combination, as when carbon di-sulphide is formed from carbon and sulphur, but perhaps not always so well remembered in the case of purely physical combination. But if we bring some Calais sand, for instance, into a solution of paraffin wax and dry it afterwards, every particle of the sand will be coated with the wax, and this purely physical combina-

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tion will neither be wetted by water, as the sand is, nor will it float in water, as paraffin wax does. Why, therefore, should we need new theories to explain the fact that a combination of hide and tanning agent shows properties different from the qualities of either? To the so-called "auto-process," which the anonymous writer thinks so full of difficulties of explanation, I shall come back a little later.

Now let us come to the root of these many misconceptions. The author entirely neglects the fact that the terms "colloids and crystalloids" have a sense only in connection with or in relation to liquid. As soon as the liquid in question shows no influence on the body we are quite unable to prove whether it is a colloid or a crystalloid; in this case we can only term it amorphous or crystalline. These two terms, crystalloid and crystalline, the anonymous writer continually mixes up; in fact, he uses one for the other, especially in the last article where he speaks about the "crystalloid forms" of aluminium, chromium- and iron-hydrates, despite his own definition of crystalloids. To make the differences a little clearer, I may perhaps give the following table:—

The compound in question is:

| I. Not dissolved in the liquid. | II. Dissolved in the liquid. |
|---|---|
| *a.* And is not influenced by it. | *a.* And shows a considerable diffusive power. |
| 1. Crystalline: Diamond<br>2. Amorphous: Coal .... } in any liq. | Crystalloid: Common salt in water. |
| *b.* Holds liquid absorbed and is swollen with it. | *b.* And shows very little diffusive power. |
| Gel. Some gums in water, caoutchouc in benzene. | Sol. Metals in water, common salt in benzene. |

Of course, the characteristics given are not the only ones to be found in the relations of compounds, either gaseous, liquid, or solid, to liquids (chemical reactions excluded). But I think we need not go into further details. As the table shows, that all these terms do not mean really different properties of the bodies, but indicate different stages of solution, it is quite obvious and needs no special proof, that the same compound may occur in any of them, as in fact common salt may be obtained as crystalloid in water, as insoluble crystalline, as sol and as gel in benzene; hence we need no mysterious "insoluble semi-crys-

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talloidal state" to completely cover all our observations with the usual scheme.

One more mistake in the anonymous writer's article, which seems to have had nearly equally disturbing effects on his speculations, is that he seems not to be aware that organized bodies, as hide or cotton are, just by being organized, something very different from ordinary colloids, and that there is till now very little probability, that we shall be allowed, to compare the gelatinous precipitates in our test-tubes with the wonders which the microscope shows us as the work of the living protoplasm. It is there where the "auto-process" comes in. If you take a thread of cotton wool, which you may completely free from fat, as the anonymous writer does with the hide in question, but bring it into a bath of some glue or gum previous to drying, it will dry up stiff, unless you prevent by continuous mechanical treatment during the drying process the fine network of organized fiber from glueing together. The same is the case with hide, in which gluey substances are always present, resulting from transformation of hide-substance, and more may be formed as the drying goes on. That on repeated soaking and drying the leather gets more supple and permanent, we may explain in different ways, of which I would prefer the idea, that in fresh hide there are some chemical constituents more easily transformed into glue-like substances, and ultimately removed by repeated soaking and drying.

Now, I will lastly show the positively false statements. They are to be found in the part of the article which deals with alum-tannage. The anonymous writer says: "The mineral tanning agents are hydrates," though Eitner showed already long years ago that the chrome-tanning agent is a basic chromium salt, and Stiasny showed more especially that it is usually basic sulphate; and though it is theoretically impossible that hydrates tan, because, being in colloidal solution, they cannot penetrate into a gel. What penetrates, therefore, can only be a crystalloid, speaking of mineral tannage only, without mechanical treatment, which of course, after being fixed by the absorptive power of the fiber, may undergo further changes by further hydrolysis on washing or neutralizing. He says later on that washing the hide does not lose very much of the alum, but is freed from the

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acid portion; though it is known to every glove-kid manufacturer that washing removes a very great amount of alumina salt more than remains in the skin; though it would be impossible, as it really not is, to bring alum leather back to the pelt state simply by prolonged washing, if the alum were hydrolyzed into alumina-hydrate and acid; and though neither alumina nor chrome leather is "freed" from the acid portion a fair amount of acid always remaining in combination with the base. I hope shortly to publish the results obtained by myself in the case of alumina-glove-kid.

Yours faithfully,

DR. MAX GOLDMAN.

Leather Industries Department,
Leeds University.

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DEAR SIR:—

I have not maintained as the anonymous writer appears to indicate, that one and the self-same substance cannot exist in both crystalloidal and colloidal forms. On the other hand, I have given an example of this in the two forms (A and B) of silicic acid. I am also of the opinion that crystalloids and colloids do not form two classes of substances abruptly separated from one another. There are countless transitional forms connecting these two great states, and the position which these forms stand in relationship to one another depends upon the way one looks at them. This is specially evident in the case of the hydrosols, more particularly the scarcely-developed very soluble colloids. If one chooses for a characteristic difference between crystalloids and colloids the difference in velocity of diffusion, one finds all possible innumerable transitional states between pure crystallizable salts and pure colloidal albumen. If we choose the influence of soluble substances upon the vapor pressure (lowering of the boiling point, etc.), we find again an unbroken line of substances, the order of which will in no way be the same as that found by employing the velocity of diffusion test. Yet, again, other characteristics may be taken (Tyndal phenomenon, viscosity, behavior in an electric field, etc.), showing additional transitional forms and a different classification.

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These transitions are of great interest to the tanner, for vegetable tanning materials are distinguished by a considerable rate of diffusion, and by considerable insensibility to electrolysis. Yet with regard to the bigness of the molecules and influence of the vapor pressure they behave as colloids.

I would thus first put right the incorrect translation of my criticism with regard to my article in *Der Gerber*, and give my view of the question.

What I criticized in the theory of tanning of your author was his view that change from hide to leather could be regarded as a transition of a colloid to a crystalloid. This I consider is an unprovable and arbitrary opinion. Arbitrary likewise are the specified examples of the transitions of colloids to crystalloids given in the table. I should like to know the reasons for so classifying them, for no doubt reference was made to original publications in writing the article. I wish also to mention that an insoluble crystalloidal form of tan is unknown to me, as is also a soluble crystalloidal form of aluminium hydroxide. In the explanation of the transition of an organic substance from a colloid to a crystalloid, your writer says:—"Where, in organic chemistry there exist two forms—colloidal and crystalloidal—of the same substance, the colloidal form is always soluble and the crystalloidal form insoluble. Of the two forms the colloid is the unstable, non-permanent one, and either time or some slight upsetting influence such as drying or slight warming may be sufficient to bring about a change of state to the crystalloidal condition."

This seems to me to show a confusion between jelly-formation and a change to crystalline form. In the numerous cases where a soluble colloid changes to an insoluble form through drying or warmth such change is to be considered as a gelatinous form of the substance in question, and therefore as a colloid.

As the change of hide to leather was similarly expressed—*i. e.*, the change from a form subject to solution and hydrolytic agencies to a stable form—the impression is given that this misunderstood conception of the forming of a hydrogel has been the cause of the new tanning theory. However this may be,

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the conception of the tanning process as a change of a colloidal hide into a more crystalloidal form must remain so far incorrect until some proof in favor of the crystalloidal nature of the leather can be produced, and such proof will probably never be forthcoming.

Lastly, with regard to the quoted article of Earp, it must be stated that it has a great similarity with the views above expressed. Earp remarked with regard to gelatine sterilized with heat that in a few days an increasing insolubility in water occurred. He calls this state insoluble and crystalline-like. To prove this crystalline-like nature Earp still has to do.

Yours truly,
PROF. W. EDMUND STIASNY.

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DEAR SIR:—

My attention has been called to some criticisms which have appeared in foreign publications on some of the ideas with regard to tanning which have appeared in this column. These criticisms are always welcome, whether adverse or otherwise. It is the special business and privilege of the writer to investigate and pronounce opinions upon the theories formulated by scientists from time to time with regard to the principles which underlie the tanning of hides, and no duty can be performed which is more useful to readers of this column than examining outside criticisms which may appear on our own theories. I do not always envy some of the critics the assurance with which they plunge into the question, and I can only come to the conclusion that they write without having a full grasp of the subject.. In an article in *Der Gerber* (802, p. 33), for instance, Professor E. Stiasny adopts a somewhat peculiar style of scientific criticism. In referring to the writer's article in these columns he states, "The author goes on to the discussion of the nature of the crystalloidal and colloidal states, and here we find intrinsic error." Surely this is a bold and futile statement to make unless the professor shows where the error is to be found, and this he does not do.

I am aware that some people still say that the earth is a flat surface, and probably a great many more will say that the sun

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goes round the earth. Such statements are generally made by those whose knowledge of physical laws is not sufficient to enable them to grasp anything beyond these. The Professor seems to have made his erroneous statements on my article from a similar cause. He appears to be unable to grasp anything beyond a hydrogel. That this is so is indeed proved from his own example, which he gives to show that a substance exists in two forms, crystalloidal and colloidal. The crystalloidal state, he quotes, (which is, by the way, not a crystalloidal state, but a solution of a presumably crystalloidal substance) changes to the colloidal gelatinous form. This is quite right, as far as it goes, but it has nothing at all to do with the theory of tanning suggested in these columns. I never considered the tanning process as an example of a soluble crystalloid changing to a gelatinous colloid. How, indeed, could anyone do so ?

Professor Stiasny only shows by this example that his ideas end with the gelatinous hydrogel condition, which is the point at which the conversion of hide substance into leather begins.

The behavior of colloids under different physical actions to which Professor Stiasny refers in his letter in this issue has also nothing to do with the theory, for like the example above, they are all relative to colloids existing in states between Professor Stiasny's limits of conception. They are true enough,, but not of interest to tanners. though within the ken of most students of experimental physics. The formation of an insoluble hydrogel from a soluble colloid is only one step in the direction towards an insoluble crystalloidal condition. It is the subsequent steps which my articles treated of.

There is, indeed, little to remark upon in Professor Stiasny's letter. He states: "I also wish to mention that an insoluble crystalloidal form of tan is unknown to me, as is also a soluble crystalloidal form of aluminium hydroxide." I may refer him to two of the former—namely, bloom and catechin—whilst the soluble aluminum hydrate he asks about is known in England as Crum's aluminium hydrate.

The whole of his letter seems to be with reference to the changes from a soluble hydrosol to an insoluble hydrogel, with which the theory of tanning under discussion has nothing to

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do, except in so far as the change from hide to leather, being, as the theory states, a change from a hydrogel to an insoluble crystalloid (or semi-crystalloid), is in the same direction, or sense, as a change from hydrosol to hydrogel. The letter is not so much a criticism of my articles as a making of bare statements and a discussion of something quite different from my theory. I submit to my readers that this is hardly the way to upset the simplest theory, or even to criticize it. I hope the Professor, who has already distinguished himself as a careful experimenter, will in future tackle my articles with all the knowledge he possesses, when I shall endeavor to meet any criticisms he may bring forward. It is my intention at some future time to enlarge on my previous articles, when I shall try to put the subject in such a form that any misconception of it by a scientist will be impossible.

Referring to the extraordinary letter of Dr. Goldmann, who begins with a sort of proem, and would like to end with a three-legged syllogism, these might be amusing, were there any originality about them. Unfortunately the one is a very ordinary platitude, whilst the other has been quite outdistanced by the boy who proved to his father that a horse chestnut was a chestnut horse, and only became disgusted with his cleverness in logic when his father presented him with a chestnut instead of a riding pony. Unless the doctor is more careful, some equally disastrous regulation of his spurious logic may overtake himself. The remainder of the doctor's letter is such a mixing and muddling up of terms, coupled with pompous announcements and strange questions, that one of my University friends suggests that I should answer it in Welsh.

I, however, think that the best possible reply to give is to advise the doctor to study and try to understand some of those text-books to which he refers. If he will master even a couple of these—one on physics and one on organic chemistry—he ought to acquire a greater knowledge of these subjects than he at present possesses. There are also many good handbooks on logic: Whateley, Mill, Jevon, and others. I also recommend the doctor to read up one of the volumes by Alexander Bain, where he might learn something about that great faculty

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which very small boys and girls possess for making pompous announcements and asking strange questions.

Yours faithfully,

THE WRITER OF THE NOTES.

## REVIEWS

**A New System of Tanning.** LE FRANC PARLEUR. Paris.—The article describes the use of a new chemical in the tanning industry. This chemical, a derivative of chloroform, is called deyrol, probably a patented article. It is claimed that skins prepared with deyrol absorb tanning materials with great rapidity and have great power of resistance. Skins thus prepared give leathers of lighter shades and preserve the suppleness of the finest skins. Briefly stated, its use is as follows: For 1000 kilos of skins (large ox-hides) prepare a solution of 20 kilos of deyrol in 4000 kilos of cold water. Immerse the skins in this solution for 48 hours raising two or three times to secure a thorough impregnation. Lift, drain, and proceed with the usual method of tanning, which, it is claimed is much shortened by said treatment. About two thirds of the deyrol is absorbed by the hides in 48 hours, after which the bath should be strengthened accordingly to maintain a uniform strength. At the end of four or five operations, the impurities which accumulate should be removed. Before treating with deyrol, the skins should be rendered as nearly lime-free as possible in the drenches, since otherwise the effect of the chemical will be partially nullified. Poorly tanned skins are brought back into good condition by soaking 48 hours in a 2-3 per cent. solution of deyrol.

**Technology of Soap.** F. GOLDSCHMIDT. *Zeits. f. Chem. u. Ind. d. Kolloide*, through *Collegium 1908*, p. 63.—A technical soap, even in its purest form does not represent the formula of a simple salt of a fatty acid as Chevreul defined it in 1838. The most striking additional ingredient is a fairly constant amount of water. Some consider this to be water of crystallization, a portion of which is more loosely bound and disappears on drying. The small amounts of salt, glycerine, etc., have been considered as impurities. Measurements of the electrical conductivity however show that the water in soap plays the role of a normal solvent, the conductivity corresponding to that of a solution of the salts regarded as impurities. The author states that the purely scientific literature of soaps is meagre and cites the more important authorities. The earlier investigators dealt with dilute solutions and only recently have systematic researches such as those of Leimdorfer and of Merklen been made upon the concentrated solutions which obtain in manufacture. The control of the chemical reaction of soap making is simple; the real labor of the soap-boiler is in securing a product of the required physical character by following empirically established rules.

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In the first stage of the manufacture in the case of fatty acids the saponification is effected with alkaline carbonates while caustic alkali is employed for the neutral fats. When the reaction is complete, a thick transparent mass is obtained, called the "soap-paste" (Seifenleim), containing an excess of alkali which is essential to practically attain a complete saponification.

In the manufacture of grained soap (Kernseife), salt is next added to the contents of the kettle until there is a separation in two layers, the upper being the soap, and the lower a soap-free saline solution, the "under-lye." When less salt is used, as in the manufacture of "settled" grain soap, the lower layer still contains more or less soap in solution; this "nigre," the German soap-boiler calls the "Leimniederschlag" (paste precipitate).

Merklen employs the phase-rule theory in the discussion of the composition of the two layers in order to find an explanation for the uniform character of commercial soap without the assumption of fixed chemical proportions. The two-phase system of soap and nigre is made up of four independent components, soap, alkali, salt and water. Pressure and temperature are in practice constant; if the amounts of two of the three components in solution are set by the manufacture, then the third is determined.

The systems in practice are more complicated, since glycerine and carbonate are also present. By systematic experiments Merklen has obtained soaps of very variable composition.

In practice "settled" grain soap is often made by the indirect method. The soap is first totally salted out and then boiled with fresh salt solution, gradually diluting producing a "nigre" on settling. Free alkali must be present in the salt water, because a hydrolytic dissociation of the soap takes place, and the product would otherwise contain free fatty acid, ultimately turning dark and becoming rancid.

Of more practical significance than Merklen's employment of the phase rule, are his conclusions based upon the colloidal character of soap solutions. In the soap-paste we have to do with colloidal bodies, the salting out being a genuine coagulation. These colloids are of variable stability, depending upon the chemical composition of the various fats employed.

Merklen has determined the limit concentrations of the saline solutions in which the soda soaps are entirely insoluble, using the composite lyes occurring in practice, containing sodium chloride, hydrate and carbonate. The results are not suited for the theoretic discussions, being complicated by too many elements. It might be thought some fractionation of the homologous fatty acids would result in the salting process, but analysis does not confirm this.

Finished soaps are to be considered as adsorption compounds, the adsorbing power of a soap depending upon four factors, (1) its own chem-

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ical composition (2) nature of the solvent (3) nature of the electrolyte, (4) the temperature.

Merklen classifies commercial soaps into

1) Plain grain soap "on under-lye," the equilibrium between soap and lye being at boiling temperature.

2) Marbled grain soap, likewise made "on under-lye," but allowed to partially cool in the kettle, salts being adsorbed; on removal from the lye and further cooling a disturbance of the system ensues and a non-homogeneous product is formed.

3) Settled grain soap, made at the boiling temperature on a nigre.

4) Paste soap (Leimseife), a solid solution of soap in a saline medium.

5) "Eschweger" soap, likewise a solution, but marbled.

A phenomenon of importance in soap manufacture is the gelatinizing of soap solutions, especially in the preparation of soft soaps (Schmierseifen). Here we have not as in grain soap, a separation but a homogeneous solidification of the entire product. The nature and concentration of the salts present are therefore of greater influence and the soap-boiler gives especial attention to the causticity of the lyes.

A special problem is offered in the manufacture of the cheaper "filled soaps" which unfortunately are so prevalent. The simplest example is the "paste soap" referred to in the classified list containing as a rule salt or potash. Another class of filled soap is obtained by adding water-glass solutions to grain soap; the filling is generally made strongly alkaline. In conclusion the filling of soft soaps is briefly considered. Potato-starch is employed, which has an extraordinary gelatinizing power through the action of alkali.

**Physical Modifications of Gelatine in Presence of Electrolytes and Non-Electrolytes.** J. L. DES BANCELS, *Compt. rend.*, 1908, 146, 290-291.—At ordinary temperature gelatine is soluble in water containing various neutral salts differing in extent of their influence. Salts of bivalent metals exert greater influence than salts of univalent metals in same concentration of solution. Nitrates of the same metal show greater activity than chlorides. Non-electrolytes, for example alcohol or acetone, and water dissolve gelatine in presence of electrolytes Some water is necessary for solution, after which the gelatine dissolves more rapidly as the amount of non-electrolyte is increased. If the salts are removed from the solution by dialysis or precipitation, the gelatine can be easily recovered.

**Contribution to the Question of the Constitution of Tannin.** M. NIERENSTEIN. *Ber. deutsch. chim. Ges.* 1908, p. 77.—The writer believes that the tannin complex consists of digallic acid (1), for which he retains the

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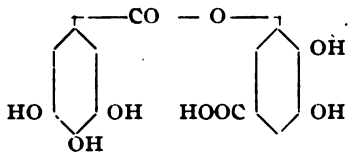
term tannin, and a hydroxylized product (II), for which he proposes the name leukotannin.

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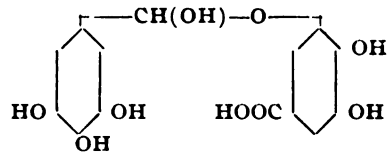


II

Experiments are described made upon the two acetyltannins, (A), m. p. 203-6°, and (B), m. p. 166°, referred to in this journal, (1907) p. 208.

Acetyltannin (A) has been already reported as giving ellagic acid on oxidation. On comparison of a similar oxidation carried out upon tri-acetylgallic acid, it was found that with acetyltannin, ellagic acid preponderated in the product, while with tri-acetylgallic acid, the yield of rufigallic acid was highest. Dekker's phthalic anhydride tannin formula on the contrary would favor the formation of rufigallic acid.

The acetyltannin (A), purified by repeated solution in alcohol to m. p. 205°, was reduced with zinc-dust in boiling glacial acetic acid solution. The product, crystallized from alcohol and precipitated with ether, fractionated into two substances;

| | M. P. | Acetyl-Value (Perkin) |
|---|---|---|
| 1. | 202-4° | 40.62 |
| 2. | 165 | 42.12 |

Computed acetyl-value for $C_{14}H_6O_9(COCH_3)_5$, 40.11. A portion of the acetyltannin (A) had therefore been reduced to acetylleukotannin (B).

Acetyl-leukotannin (B) itself remained unchanged on subjection to a similar reduction.

Acetyltannin (A) treated in pyridine solution with acetyl chloride (ice-cooling), remained unchanged.

Acetyl-leukotannin (B) under the same treatment appeared to be further acetylized. A product was obtained with m. p. 159°, acetyl-value 44.82, 44.12, 44.72; computed acetyl-value for $C_{14}H_6O_8(COCH_3)_6$, 44.41. The work will be continued.

**Wattle or Mimosa Barks.** *Bull. Imp. Inst.*, 1907, 5, 352-353.—Analyses of six samples from Cape Colony show three to be of good quality, and valued at £6 10s-£7 10s.

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| Botanical Origin | % Moisture | % Ash | % Tannin | % Non-Tannins |
|---|---|---|---|---|
| Acacia pycuantha..... | 10.14 | 1.54 | 40.09 | 13.00 |
| " decurrens (1).. | 11.36 | 1.77 | 35.36 | 12.00 |
| " " (2).. | 10.93 | 1.81 | 44.15 | 7.12 |

**Mangrove Barks.** *Bull. Imp. Inst.*, 1907, 5, 344-352.—Mangrove barks from British Honduras, British Guiana, West Africa, Portugese, East Africa, Seychelles and India, show upon analysis that the majority of specimens are suitable only for local use. Analyses of those of probable export value are given in the subjoined table. Old branches stems and roots are generally richer in tannin than young branches, etc., also the stem bark is usualy of higher value than that from branches.

| Botanical Origin | Source | % Moisture | % Ash | % Tannin | % Non-Tannins |
|---|---|---|---|---|---|
| | Portuguese E. Africa | | | | |
| | (1) Inner bark .... | 13.22 | 3.47 | 39.80 | 10.60 |
| | Outer bark ..... | 12.69 | 2.04 | 8.97 | 5.93 |
| | (2) Whole bark ... | 13.53 | 3.64 | 41.76 | 7.20 |
| *Bruguiera gymnorrhiza* | Seychelles | | | | |
| | Bark from stems . | 11.75 | 4.32 | 45.04 | 10.66 |
| | " " branches | 13.79 | 4.21 | 41.76 | 9.04 |
| *Pemphis acidula* | " " stems... | 12.06 | 6.73 | 42.54 | 9.36 |

**Moisture Contained in Skins and Leather.** P. NICOLARDOT. *Bull. Soc. Chim.*, 1908, 3, 166-173.—The "normal water" content is obtained by drying in vacuo or in air bath at 110° C. At higher temperature darkening and brittleness of the leather ensue as a result of the elimination of "water of combination." Dried at 110° C or in vacuo leather will again reabsorb its "normal water" whereas, in the latter case the reabsorption is irregular. By soaking or exposure to water vapor, leather takes up what is termed "imbibed water," which is estimated by drying in air. Leather containing either more or less than the "normal water" show a loss in tenacity, and by measurement of this tenacity we may distinguish between normal and imbibed water. A skin with its "normal water" content has less volume than the total volume of dry skins and "normal water." The author supports the view that this necessary water is "water of hydration" held by other forces than those of osmosis and capillarity. Similar skins from same locality, and subject to same atmospheric conditions have different "normal water" content, which also is influenced by the sex of the animal. Harness leather subjected to a temperature of —50° C, gained rather than lost in tenacity by the freezing of the contained water, indicating that the normal water is not simply a physical combination.

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The author's proposed method for the determination of moisture in leather is, first to extract with chloroform, dry from 3 to 4 hours at 100° -110° C and make correction for the loss involved by the removal of the fat. Results accurate within 0.5 per cent. and 2.0 per cent. higher than method of drying 48 hours in vacuo. The chloroform assists by its dehydrating and contracting action as well as by its removal of the fats.

**The Use of Rabbit Skins for Shoes.** LE FRANC PARLEUR.—Practical tests on shoes made from tanned or chromed rabbit skins have recently been made in Silesia with very flattering results. In two six month's walking tests the shoes made from rabbit skins held up equally well with those made from ordinary leather. In another test covering a period of eighteen months, the shoes made from rabbit skins made even a better showing than those made from regular leather.

**Banana Tannin.**—A Hamburg paper announces that banana tannin may be a possible industry of the future. In obtaining the hemp from a variety of banana, known as *musa textilis*, the expressed juices have been found to contain a certain amount of tannin, which if recovered, might materially enhance the value of banana plantations.

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## PATENTS

**Process of Treating Hides: U. S. Patent No. 883,124,** to F. R. WESSA, Norwood, Ohio.—An improved method of manufacturing enameled leather, involving the use of a series of permanently located frames.

**Process for the Preparation of Skins for Making Leather: French Patent No. 383,273,** to E. LE CONTE.—A preliminary treatment with a dilute solution of sulphurous acid.

**Manufacture of Glue: U. S. Patent No. 883,722,** to I. KITSEE, Philadelphia, Pa.—Means of producing a continuous sheet of glue; by causing the liquid glue to fall in a continuous thin stream and during its fall removing the surplus moisture. The so-formed thin sheet is wound around a reel, the different layers being separated by a continuous sheet of paper.

**Preparation for Use in Tanning: English Patent No. 13,879,** to P. L. ASLANOGLON SMYRNA.—An extract of valonia partially decolorized by treatment with sulphur dioxide in a water-heated digester.

**Instrument for Measuring the Thickness of Leather and Other Sheet Material: U. S. Patent No. 883,831,** to J. ROBERTSON, WOBURN, and J. S. DELANEY, Somerville, Mass.—An improved leather-gauging machine.

**Thickness-Measuring Attachment for Machines Measuring the Areas of Surfaces: U. S. Patent No. 883,832,** to J. ROBERTSON, WOBURN, and J. S.

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DELANEY, Somerville, Mass.—An attachment of the device covered by the preceding patent, for leather-measuring machines.

**Manufacture of Leather: French Patent No. 383,361,** to S. H. KNIGHT AND C.D. LIGHTBAND.—The membrane of the stomachs of animals is tanned, washed, and dyed, forming a leather having a wrinkled surface, and which is used for decorative purposes.

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## SOME OBSERVATIONS ON THE PLUMPING OF HIDES.

*By R. W. Griffith and A. A. Claflin.*

As the tanning industry gradually emerges from a state where guess work guided by practical experience and certain rule of thumb tests is the universal custom, to a condition when the individual tanner seeks the assistance of the chemist in forming his judgment, there is developed a line of chemical work known as Tannery Control. This is yet in its infancy. To a very large degree, work in "leather" chemistry has been thus far devoted to the development of methods of analysis and the determination of their relative accuracy. There has been as yet no extensive investigation as to how far the results of these analytical methods are of value to the tanner, and there is a well founded belief among practical tanners that much is yet to be learned in this respect. In the manufacture of sole leather by a sort of general consent the work of the chemist in tannery control has been mainly confined to the determination of the percentage of tannin and total acidity in the various tan liquors. Some years ago one of us in collaboration with Mr. John Youl did some work on the measurement of relative leather-forming value of different tanning materials, which proved of great interest to the practical tanner and opened up a considerable field for research on the part of the chemist.

This paper will outline some work that has been begun on the value of the acid determination in its relation to the tanner. For a long time it has been known that leather could not be made from pure Tannin or in other words that the non-tannic constituents of a Tan liquor are essential, and among the most important, if not the most important of these non-tannins are the acids which are principally Lactic and Acetic Acids. These acids are produced by the fermentation of other non-tannins, presumably of glucose-like character.

The hastening of the tanning process with the consequent lack of time for the development of natural fermentation acids, and the introduction of tannin materials like Quebracho which have only a small relative amount of glucose-like constituents has led to the use of considerable quantities of commercial

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Lactic Acid for acidifying tan liquors or as it is technically termed a plumping agent. The function of an acid in tanning, it being understood, is to swell or plump the hide and counteract the astringent action of the tannin.

Rather extensive observations have shown that by the use of commercial Lactic Acid a plumping is obtained much greater generally than that obtained by an equal or even far greater amount of the naturally occurring acids. Yet abundant analysis shows that the natural acids of the tan liquor are Lactic and Acetic Acid. Our attention is thus directed to the consideration of the other non-tannin constituents of the tan liquors and our own observations are supported by chemists of very extended experience in tannery practice, that in general there is no constant relation between the percentage of acidity in a tan liquor and the plumping of a hide.

Prof. Proctor has considered in his "Principles of Leather Manufacture" the phenomena of "plumping" caused by acids and his results show in general that plumping is in proportion to the concentration of the Hydrogen "ion," inasmuch as the addition of a salt counteracts the plumping.

Our work has been directed to the measurement of the degree of plumping produced by acids and the influence of various substances on such plumping.

It should be noted that as the Hydrogen "ion" is apparently the active agent in plumping by acids, that the increase or gain in plumping does not correspond in exact ratio to the increase in concentration of the acids themselves, thus the plumpness in 24 hours obtained with a 1/10 per cent. solution of Lactic Acid showed a gain of 21 per cent., a ½ per cent. solution a gain of 96 per cent. and a 1 per cent. solution a gain of only 122 per cent. on the original pelt.

The method devised to measure plumping has been that of measuring the displacement of water by a small piece of hide before and after it was submitted to the action of the various solutions.

The results thus far obtained indicate: that the speed with which acids plump is in direct proportion with the concentra-

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tion of the Hydrogen ion, *i. e.*, with their strength. This is not of great practical importance as in general the deleteriousness of an acid to leather is also in direct proportion to its strength. Further ½ of one per cent. Lactic Acid solution, which is the weakest acid tried, gave a more than practical plumping in 24 hours, when its action was undeterred by extraneous substances.

We were unable to discover that either gelatine or glucose in acid solutions by themselves affected the plumping of the hide, but in the presence of salt these substances seem to increase the tendency of the salt to retard the plumping of the hide.

That all salts have a deterrent effect on plumping and that the degree of this effect is dependent both on the nature of the salt and of the acid used.

It should of course be noted here that when we speak of a salt and an acid that it must be recognized that the salt and acid mutually interact, that is consider the salts and acids ionically.

The salts thus far experimented with have been Di Sodium Phosphate and Sodium Lactate.

The acids used have been Sulphuric, Formic and Lactic. In one half per cent. solutions of these acids 2½ per cent of Sodium Lactate prevented all plumping, while 2½ per cent. of Di Sodium Phosphate prevented plumping with Formic and Lactic Acid, but not with Sulphuric Acid.

Some head handler liquors from two or three tanneries were analyzed and found to contain an ash which would correspond to from 2 to 2½ per cent. Calcium Lactate.

A handler liquor in particular which had the following composition:—

| | |
|---|---|
| Total Soluble | 10.00 |
| Tannin | 3.50 |
| Non-Tannins | 6.50 |

and an acidity of 0.5 per cent., contained an ash which corresponded to 2 per cent. Calcium Lactate and showed absolutely no plumping on a piece of hide left in it for 24 hours.

An artificial non-tanning liquor composed of glucose, gelatine, organic salt and acid in the same proportions as the above

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handler liquor was prepared, and that also failed to produce any plumping in a piece of hide introduced into it.

From the point of view of practical importance it would seem that our results indicate the necessity of carrying as little lime as possible in the hide into the tan liquors.

The popular tendency is to depend upon the natural acidity of the tan liquors to neutralize and dissolve the lime, thereby increasing the presence of those salts which it has been shown retard the plumping of the hide. It is not until the point of neutralization between the acids and the lime has been passed that any plumping of the hide can possibly take place and with the constantly increasing use of materials which do not generate acidity, the maximum practical plumping of a hide is seldom reached.

The wisest precaution would be to remove as much of the lime as possible out of the hide in the beam-house and then to insure that the tail-handlers are of such acidity as to plump the fibres of the hide, rather than to have the acidity at the head, when the fibre, owing to the absorption of tannin, is not as sensitive to the influence of weak organic acids.

Another interesting phase of the question which further complicates it, is the presence of mineral salts in tannin extracts. In their efforts to produce extracts which impart a light color to leather, manufacturers are resorting to the use of inorganic salts, and the presence of these in the tan liquors more especially in the handlers is detrimental to the plumping of the hide.

## PRELIMINARY WORK ON THE EXTRACTION OF SUMAC AND MYRABOLAMS.[1]

*By Charles Eachus.*

In order to test different methods of extraction the chairman sent two samples of sumac and one sample of myrabolams to the members of the committee. Sumac number 1 was pure, and sumac number 2 was adulterated with 25 per cent., or more lentiscus. The following directions were also sent to the committee.

[1] Preliminary Report of the 1908 Committee.

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*Directions for Analysis of Sumac No. 1.*

Study No. 1.

Dry, extract, and analyze sample according to the method of the A. L. C. A. for crude materials. Report on dry basis and air dry basis.

Study No. 2.

A. Dry 100 grams of sample at a temperature between 90 and 100°C. from 3 to 12 hours. Reweigh and determine moisture.

B. Use 20 grams of material dried as in A., with 2000 cc. water for the extraction. Use an extractor similar to the Reed or Teas extractors by which a portion of the extractive solution can be drawn off at the beginning and then the extraction can be continued reflux. Use a thin wad of cotton to prevent fine material passing through. Pour 20 grams of dried sample on this and cover sample with about 100 cc. of water. Let stand one hour, instead of over night. Light burner under the extractor and run off 2000 cc. of the extractive solution, through the upper outlet tube of the extractor, collecting all of the 2000 cc. in a flask outside the extractor. Run the extraction so as to require between 6 and 8 hours for the 2000 cc. to pass over.

C. Take 20 grams dried sample with 2000 cc. water as before. Collect 1500 cc. extractive solution outside through upper tube of extractor. Run the remaining 500 cc. reflux for 14 hours.

D. Take 20 grams dried sample and 2000 cc. water as before and collect 1500 cc. extractive solution outside through lower tube of the extractor. Run remaining 500 cc. reflux for 14 hours.

Study No. 3.

Extract 20 grams dried sample with 2000 cc. water according to the method described in Prof. Procter's L. I. L. B., page 102. The extractor consists of an ordinary beaker placed in a water-bath. A common thistle tube is bent so as to form a siphon and the head of the thistle tube is covered with fine muslin, or silk. The head of the thistle tube covered thus is placed in the beaker and covered about one inch with washed

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sand and water is poured on this. The other end of the thistle tube fitted with rubber tubing and screw pinch-cock is connected with a 2000 cc. receiving flask. The liquor is started siphoning cold at first, but the temperature is gradually raised until 1000 cc. solution are through in 2 or 3 hours and the temperature is near 70° C. Then the temperature is brought to boiling point and the remaining 1000 cc. run through in 2, or 3 hours. Boiling hot water must be poured on the extractive material in the beaker during the last half of the extraction. In each case let extractive solution cool over night and analyze as per the official method of the A. L. C. A. for extracts. In each extraction test the last portion of the extractive solution with gelatine for tannin by the best method you know of and give your method.

Special Study No. 4.

After extracting sample according to study No. 3 by Procter's method run an additional 2000 cc. of boiling water through the 20 grams of extracted material. Concentrate this to a small volume and determine soluble solids and non-tannins as in extracts, but use only 10 grams of hide powder.

*Direction for Analysis of Sumac No. 2.*

Dry, extract and analyze according to direction under study No. 1, 2D, and study No. 3, for sumac No. 1.

*Directions for Analysis or Myrabolams.*

Dry, grind, extract and analyze as directed under sumac, Study No. 1, Study No. 2, A, B, C, D, and study No. 3 for sumac No. 1.

The results from six members of the Committee are as follows:—

SUMAC 1—TABLE 1.

| | Official Method. | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Analyst | Total solids | Soluble solids | Insoluble | Non-Tannin | Tannin on dry basis | Hours extracted outside | Hours extracted continuous | Presence of tannin in extracted material |
| Fox..... | 60.50 | 56.21 | 4.29 | 21.55 | 34.66 | 2 | 14 | none |
| Wilson... | 57.35 | 53.39 | 3.97 | 20.53 | 32.86 | · | 8 | none |
| Mosser... | 56.42 | 52.35 | 4.07 | 20.51 | 31.84 | 4 | 14 | none |
| Russell .. | 56.05 | 53.62 | 2.43 | 20.46 | 33.16 | 4 | 3 | none |
| White.... | 50.13 | 48.59 | 1.54 | 19.11 | 29.48 | 7½ | .. | cloudy |
| Eachus .. | 56.30 | 55.06 | 1.24 | 21.40 | 33.66 | 4 | 14 | none |

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## SUMAC 1—TABLE 2 B.

2000 cc. Extracted Outside With Teas or Reed Extractor.

| Analyst | Total solids | Soluble solids | Insoluble | Non-Tannin | Tannin on dry basis | Hours extracted outside | Hours extracted continuous | Presence of tannin in extracted material |
|---|---|---|---|---|---|---|---|---|
| Fox..... | 51.50 | 50.25 | 1.25 | 18.15 | 32.10 | 4½ | | slight |
| Russell.... | 55.53 | 53.32 | 2.21 | 20.51 | 32.81 | 7 | | none |
| Mosser .... | 52.20 | 49.75 | 2.45 | 20.12 | 29.63 | 8 | | distinct |
| Wilson.... | 55.17 | 52.41 | 2.76 | 19.65 | 32.76 | 8 | | distinct |
| White..... | 53.70 | 51.08 | 2.62 | 19.33 | 31.75 | 6 | | slightly opalescent |
| Eachus.... | 52.00 | 51.17 | .83 | 19.06 | 32.11 | 5 | | slight |

## SUMAC 1—TABLE 2 C.

1500 cc. Extracted Outside Through Upper Tube. Teas or Reed Extractor. 500 cc. Continuous.

| Analyst | Total solids | Soluble solids | Insoluble | Non-Tannin | Tannin on dry basis | Hours extracted outside | Hours extracted continuous | Presence of tannin in extracted material |
|---|---|---|---|---|---|---|---|---|
| Fox..... | 57.40 | 54.20 | 3.20 | 20.35 | 33.85 | 4½ | 12½ | none |
| Russell..... | 59.34 | 55.39 | 3.95 | 22.01 | 33.38 | 3 | 14 | none |
| Mosser..... | 58.60 | 55.00 | 3.60 | 20.98 | 34.02 | 4 | 14 | none |
| Wilson..... | 59.63 | 55.04 | 4.59 | 21.37 | 33.67 | 5 | 14 | none |
| White..... | 58.02 | 51.26 | 6.76 | 21.17 | 30.09 | 6 | 14 | none |
| Eachus .... | 55.20 | 54.04 | 1.16 | 20.20 | 33.84 | 4 | 14 | none |

## SUMAC 1—TABLE 2 D.

1500 cc. Outside Through Lower Tube. Teas or Reed Extractor. 500 cc. Continuous.

| Analyst | Total solids | Soluble solids | Insoluble | Non-Tannin | Tannin on dry basis | Hours extracted outside | Hours extracted continuous | Presence of tannin in extracted material |
|---|---|---|---|---|---|---|---|---|
| Fox ..... | 59.45 | 55.50 | 3.95 | 20.82 | 34.68 | 4½ | 12½ | no test |
| Russell... | 60.08 | 56.03 | 4.05 | 21.46 | 34.57 | 3 | 14 | no test |
| Mosser ... | 59.30 | 55.00 | 4.30 | 22.77 | 32.23 | 4 | 14 | no test |
| Wilson..... | 59.57 | 55.57 | 4.00 | 20.88 | 34.69 | 5 | 14 | no test |
| White.... | 57.93 | 52.76 | 5.17 | 20.09 | 32.67 | 6 | 14 | no test |
| Eachus... | 56.30 | 55.24 | 1.06 | 20.74 | 34.50 | 4 | 14 | none |

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## SUMAC 1—TABLE 3.

2000 cc. Extracted in Percolator According to Procter.

| Analyst | Total solids | Soluble solids | Insoluble | Non-Tannin | Tannin on dry basis | Hours extracted outside | Hours extracted continuous | Presence of tannin in extracted material |
|---|---|---|---|---|---|---|---|---|
| Fox ..... | 50.70 | 49.63 | 1.07 | 18.44 | 31.19 | 4½ | .. | strong |
| Russell.. | 50.55 | 47.68 | 2.87 | 18.58 | 29.10 | 8 | .. | none |
| Mosser .. | 49.10 | 47.35 | 1.75 | 17.25 | 30.10 | 9 | .. | distinct |
| Wilson .. | 52.20 | 50.48 | 1.72 | 18.65 | 31.83 | 6 | .. | distinct |
| White ... | 50.35 | 48.65 | 1.70 | 19.47 | 29.18 | 7 | .. | trace |
| Eachus.. | 50.40 | 49.74 | .66 | 18.20 | 31.54 | 8 | .. | trace |

## SUMAC 1—TABLE 4.

2000 cc. Hot Water Run Through Extracted Material From Sumac 1. Table 3.

| Analyst | Soluble solids | Non-Tannin | Tannin on dry basis | Hours extracted outside | Presence of tannin in extracted material |
|---|---|---|---|---|---|
| Fox..... | 1.76 | 1.34 | .42 | 2 | very slight trace |
| Russell ..... | 1.60 | .91 | .69 | 8 | slight |
| Mosser..... | .88 | .44 | .44 | 4 | slight |
| Wilson..... | 2.32 | 1.59 | .73 | 6 | none |
| White ..... | 3.08 | 2.36 | .72 | 6 | none |
| Eachus ..... | 1.88 | 1.40 | .48 | 8 | none |

## SUMAC 2—TABLE 1.

Official Method.

| Analyst | Total solids | Soluble solids | Insoluble | Non-Tannin | Tannin on dry basis | Hours extracted outside | Hours extracted continuous | Presence of tannin in extracted material |
|---|---|---|---|---|---|---|---|---|
| Fox..... | 54.90 | 51.01 | 3.89 | 21.65 | 29.36 | 2 | 14 | none |
| Russell... | 50.53 | 47.52 | 3.01 | 20.75 | 26.77 | 4 | 3 | none |
| Mosser... | 49.46 | 44.58 | 4.88 | 22.61 | 21.97 | 4 | 14 | none |
| Wilson... | 52.82 | 49.24 | 3.58 | 19.73 | 29.51 | . | 8 | none |
| White ... | 45.10 | 43.77 | 1.33 | 19.42 | 24.35 | 7½ | .. | cloudy |
| Eachus .. | 50.90 | 49.80 | 1.10 | 21.40 | 28.40 | 4 | 14 | none |

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## SUMAC 2—TABLE 2 D.

1500 cc. Outside Through Lower Tube. Teas or Reed Extractor. 500 cc. Continuous for 14 Hours.

| Analyst | Total solids | Soluble solids | Insoluble | Non-Tannin | Tannin on dry basis | Hours extracted outside | Hours extracted continuous | Presence of tannin in extracted material |
|---|---|---|---|---|---|---|---|---|
| Fox..... | 53.25 | 49.95 | 3.30 | 20.87 | 29.08 | 4½ | 12½ | none |
| Russell..... | 52.64 | 49.63 | 3.01 | 22.75 | 26.88 | 3 | 14 | none |
| Mosser..... | 53.35 | 49.30 | 4.05 | 22.77 | 26.53 | 4 | 14 | none |
| Wilson..... | 55.30 | 49.81 | 5.49 | 21.38 | 28.43 | 5 | 14 | none |
| White..... | 53.44 | 49.62 | 3.82 | 22.59 | 27.03 | 6 | 14 | none |
| Eachus..... | 50.78 | 50.24 | .54 | 21.04 | 29.20 | 4 | 14 | none |

## SUMAC 2—TABLE 3.

2000 cc. Extracted by Percolation According to Procter.

| Analyst | Total solids | Soluble solids | Insoluble | Non-Tannin | Tannin on dry basis | Hours extracted outside | Presence of tannin in extracted material |
|---|---|---|---|---|---|---|---|
| Fox ..... | 46.10 | 44.20 | 1.90 | 19.37 | 24.83 | 4½ | strong |
| Russell ..... | 49.07 | 46.41 | 2.66 | 19.01 | 27.40 | 8 | none |
| Mosser ..... | 45.00 | 43.35 | 1.65 | 17.82 | 25.53 | 9 | distinct |
| Wilson ..... | 46.35 | 44 78 | 1.57 | 18.72 | 26.06 | 6 | strong |
| White ..... | 44.29 | 43.15 | 1.14 | 19.16 | 23.99 | 7 | trace |
| Eachus ..... | 45.20 | 44.40 | .80 | 19.16 | 25.24 | 8 | trace |

## MYRABOLAMS—TABLE 1.

Official Method.

| Analyst | Total solids | Soluble solids | Insoluble | Non-Tannin | Tannin on dry basis | Hours extracted outside | Hours extracted continuous | Presence of tannin in extracted material |
|---|---|---|---|---|---|---|---|---|
| Fox..... | 52.63 | 51.15 | 1.48 | 16.23 | 34.92 | 2 | 14 | none |
| Russell..... | 45.40 | 43.53 | 1.87 | 12.80 | 30.73 | 4 | 3 | none |
| Mosser..... | 51.30 | 48.46 | 2.84 | 15.46 | 33.00 | 4 | 14 | none |
| Wilson..... | 53.74 | 51.55 | 2.19 | 14.81 | 36.74 | . | 8 | none |
| White..... | 48.79 | 47.31 | 1.48 | 14.80 | 32.51 | 8 | .. | none |
| Eachus..... | 51.07 | 48.60 | 2.47 | 14.06 | 34.54 | 4 | 14 | none |

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## MYRABOLAMS—TABLE 2 B.

2000 cc. Extracted Outside With Teas or Reed Extractor.

| Analyst | Total solids | Soluble solids | Insoluble | Non-Tannin | Tannin on dry basis | Hours extracted outside | Presence of tannin in extracted material |
|---|---|---|---|---|---|---|---|
| Fox ..... | 49.70 | 48.30 | 1.40 | 12.67 | 35.63 | 4½ | none |
| Russell..... | 46.67 | 45.11 | 1.56 | 12.18 | 32.93 | 7 | none |
| Mosser ..... | 50.40 | 47.60 | 2.80 | 13.90 | 33.70 | 8 | slight |
| Wilson . ..... | 52.58 | 50.73 | 1.85 | 13.10 | 37.63 | 8 | strong |
| White ..... | 50.53 | 47.63 | 2.90 | 13.00 | 34.63 | 8 | none |
| Eachus ..... | 48.90 | 48.10 | .80 | 14.61 | 33.49 | 6 | none |

## MYRABOLAMS—TABLE 2 C.

1500 cc. Extracted Outside Through Upper Tube. Teas or Reed Extractor and 500 cc. Continuous 14 Hours.

| Analyst | Total solids | Soluble solids | Insoluble | Non-Tannin | Tannin on dry basis | Hours extracted outside | Hours extracted continuous | Presence of tannin in extracted material |
|---|---|---|---|---|---|---|---|---|
| Fox..... | 51.35 | 48.95 | 2.40 | 13.80 | 35.15 | 4½ | 12½ | none |
| Russell... | 54.15 | 51.65 | 2.50 | 14.38 | 37.27 | 3 | 14 | none |
| Mosser... | 51.35 | 48.70 | 2.65 | 15.12 | 33.58 | 4 | 14 | none |
| Wilson... | 58.67 | 55.85 | 2.82 | 15.61 | 40.24 | 5 | 14 | none |
| White.... | 51.09 | 48.46 | 2.63 | 13.76 | 34.70 | 6 | 14 | none |
| Eachus... | 51.10 | 48.70 | 2.40 | 14.10 | 34.60 | 4 | 14 | none |

## MYRABOLAMS—TABLE 2 D.

1500 cc. Extracted Through Lower Tube. Teas or Reed Extractor, and 500 cc. Continuous 14 Hours.

| Analyst | Total solids | Soluble solids | Insoluble | Non-Tannin | Tannin on dry basis | Hours extracted outside | Hours extracted continuous | Presence of tannin in extracted material |
|---|---|---|---|---|---|---|---|---|
| Fox..... | 50.55 | 48.70 | 1.85 | 13.27 | 35.43 | 4½ | 12½ | none |
| Russell... | 54.26 | 50.70 | 3.56 | 15.03 | 35.67 | 3 | 14 | none |
| Mosser... | 51.90 | 48.80 | 3.10 | 14.93 | 33.87 | 4 | 14 | none |
| Wilson... | 59.19 | 56.14 | 3.05 | 16.19 | 39.95 | 5 | 14 | none |
| White.... | 51.75 | 49.79 | 1.96 | 13.38 | 36.41 | 6 | 14 | none |
| Eachus... | 50.50 | 48.70 | 1.80 | 13.44 | 35.26 | 4 | 14 | none |

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MYRABOLAMS—TABLE 3.

2000 cc. Extracted by Percolation According to Procter.

| Analyst | Total solids | Soluble solids | Insoluble | Non-Tannin | Tannin on dry basis | Hours extracted outside | Hours extracted continuous | Presence of tannin in extracted material |
|---|---|---|---|---|---|---|---|---|
| Fox ..... | 48.55 | 47.80 | .75 | 13.91 | 33.89 | 4½ | .. | none |
| Russell .. | 44.14 | 42.66 | 1.48 | 12.10 | 30.56 | 8 | .. | none |
| Mosser .. | 46.30 | 44.20 | 2.10 | 12.65 | 31.55 | 9 | .. | distinct |
| Wilson .. | 53.46 | 51.89 | 1.57 | 14.33 | 37.56 | 6 | .. | distinct |
| White ... | 48.80 | 47.25 | 1.55 | 13.38 | 33.87 | 7 | .. | none |
| Eachus .. | 46.55 | 45.40 | 1.15 | 12.20 | 33.20 | 4 | 14 | trace |

The samples were thoroughly mixed so that no error would arise from that source, but the results obtained by the different members of the committee show that different methods of extraction give widely varying results and also that different chemists get widely varying results using the same method. Mr. Fox states that different amounts of hide powder used with the solutions that were boiled reflux gave wide variations in non-tannins, while with solutions collected outside the variations in non-tannins are not so great. The official amount of hide powder did not give clear non-tannins with solutions boiled reflux. Mr. Fox also says that drawing the solutions through the lower tube of the extractor gives higher tannin in all cases, due probably to the water not getting a chance to cool off in the extractor before it strikes the material in the bottom of the extractor.

Mr. Russell says, "I do not see that any definite conclusion can be drawn favoring any of the methods outlined. The simple percolation method of Proctor does not seem efficient enough, as I found tannin in special study 5 after twice the usual amount of water had percolated over. On the other hand the harsher forms of extraction must be viewed with suspicion as to whether the tannin that shows up analytically by these methods is really tannin. Are we going to consider everything capable of being absorbed by hide powder as tannin?

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The present official method could be made applicable to nearly every sort of crude material if it were modified to permit of an hours digestion of the material before extraction and if an amount of material were prescribed which would require two liters of water to give a liquor of the official strength. In this way the method would be modified in no radical manner and the proportion of tannin subjected to the continuous extraction would be very materially lowered. The time of extraction for a two liter liquor does not need to be much greater than for one liter."

In Mr. Russell's study No. 5 he extracted the residue from special study No. 4 for three hours by continuous extraction in a Teas extractor and found 1.19 per cent. tannin on the absolutely dry basis. He also gives some suggestions in regard to the difficulty of sampling myrabolams, which will be attended to in the final report.

Mr. Mosser says that he prefers method No. 2C, because it requires very little attention and seems to get the maximum amount of soluble matter without distroying any tannin. He also thinks that the time for running reflux could be greatly shortened, as there was no test for tannin at the end of three hours for the myrabolams and five hours for the sumacs.

Mr. Wilson says that the results are so much at variance that he does not care to comment upon them, but methods 2C and 2D are to be preferred.

Mr. White objects to extracting reflux for 14 hours and he prefers a method like 2D in which the extraction, reflux and all can be made in one day in a Teas Extractor.

All the members of the committee think that the percolation method gives too low results and that it requires too much attention. The Teas side tube extractor was used by all the members of the committee and it seems that an easily manipulated method using some such form of extractor is to be desired.

In conclusion the chairman wishes to state that he agrees with all the members of the committee in their criticisms, and will withhold further suggestions until the final report.

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## ACID IN LEATHER DYEING: ITS ABSORPTION AND EFFECT.

*By M. C. Lamb, F. C. S., and J. W. Lamb.*

PART I.

It has long been known as a practical fact that the critical temperature when dyeing leather, using acid dyes with an addition of acid to the dyebath, was about 50° C., and that when this temperature was exceeded by more than three or four degrees serious injury by disintegration and shortening of the leather fibre was likely to take place, the leather being rendered hard, brittle, and in many cases quite unsaleable.

In order to ascertain what influence the amount of acid in the dyebath possessed, the temperature at which apparent tendering of the leather was brought about, and the acids which possessed the least detrimental action, it was thought well to carry out a systematic series of experiments.

It is well known that the only acids which can be successfully employed as additions to the dyebath when dyeing leather with acid colors when a full shade of color is required are sulphuric, hydrochloric, oxalic, and formic acids.

In the first experiments a well-tanned oak bark calf skin was prepared as is customary before dyeing by scouring with soap solution to remove the ellagic acid deposited during the tanning, the said deposit being commonly termed "Bloom." After scouring the leather was washed, sumached, and struck out, and then dried. The skin was cut up into pieces of equal size (5 ins. by 4 ins.). The pieces of leather for each experiment were taken as far as possible from the same portion of the skin.

In the first experiment five pieces of leather were immersed in a cold solution of the following acids: Sulphuric acid, hydrochloric acid, formic acid, oxalic acid, and sulphuric acid and sodium sulphate. Each piece of leather was immersed in 800 cubic centimeters of N/50 acid, at laboratory temperature, for one hour; then removed, allowed to drain back into the solution, and the amount of acid left in the solution was estimated by volumetric analysis in order to ascertain the amount

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of acid absorbed by the leather. The pieces of leather were afterwards carefully dried.

It was found that the amount of acid taken up in each case was as follows:—

TEMPERATURE:—15°C.

| Treatment | Amount of acid absorbed by leather in cc. N/10 solution |
|---|---|
| Sulphuric acid ($H_2SO_4$) N/50 | 62·7 |
| Hydrochloric acid (HCl) N/50 | 61·6 |
| Formic acid (H·COOH) N/50 | 22·8 |
| Oxalic acid ($C_2H_2O_4$) N/50 | 20·0 |
| Sodium sulphate and sulphuric acid ($NaHSO_4$) N/50 | 66·7 |

It will be noticed from the above that the quantities of sulphuric, hydrochloric, and the sulphuric and sodium sulphate (sodium bisulphate) mixture were taken up by the leather in about equivalent amounts, and in much greater excess than the amounts of the organic acids, which were absorbed in very small quantities at this temperature.

The experiment was now again repeated, using fresh pieces of the same kind of leather, but in this case the temperature of the solution was kept at the ordinary dyeing temperature (50° C.), the leather being immersed for one hour as before.

On removing the leather and estimating the amounts of acid remaining in the solutions, it was found that though the quantity absorbed by the leather was proportionally high as compared with the previous experiment, the affinity of the various acids for the leather remained relatively the same, the inorganic acids being absorbed in much greater amounts than the organic acids.

TEMPERATURE:—50°C.

| Treatment | Number of cc. N/10 acid absorbed by leather. |
|---|---|
| Sulphuric acid N/50 | 90·7 |
| Hydrochloric acid N/50 | 88·0 |
| Formic acid N/50 | 17·9 |
| Oxalic acid N/50 | 35·8 |
| Sodium bisulphate N/50 | 88·3 |

So far as the condition of the leather was concerned there was no apparent difference except as regards color. The leathers treated with sulphuric, oxalic, and hydrochloric acids

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were brighter and clearer in color than those treated with formic acid and the sulphuric and sodium sulphate mixture.

The next experiments were carried out with the object of obtaining further confirmatory evidence of the proportionate amounts of acids absorbed by the leather, but more particularly to note the behaviour of the leather under the action of various solutions employed at the same concentration as in the previous experiments, and at various temperatures.

Six pieces of leather were immersed in the following solutions, strength N/50, at a temperature of 55°C., and the amounts of acid absorbed found to be as follows:—

TEMPERATURE:—55°C.

| Treatment | Number of cc. N/10 acid absorbed by leather. |
|---|---|
| Water | ... |
| Sulphuric acid | 95·5 |
| Hydrochloric acid | 76·4 |
| Formic acid | 17·9 |
| Oxalic acid | 32·1 |
| Sulphuric acid + sodium sulphate | 89·8 |

the leather being immersed for one hour as before.

So far as one could judge by the appearance of the leather after drying, there had been no detrimental action on the leather fibre by the treatment. It is intended, however, later to test the various leathers for tensile strength.

After this, pieces of leather were treated in the above-mentioned solutions at temperatures of 60°, 65°, and 70°C., and gave the following results regarding absorption of acid by the leather.

| Temperature. Treatment. | 60°C. | 65°C. | 70°C. |
|---|---|---|---|
| | Number of cc. N/10 acid absorbed by leather. | | |
| Water | ... | ... | ... |
| Sulphuric acid N/50 | 90·2 | 96·6 | 93·7 |
| Hydrochloric acid N/50 | 87.5 | 84·5 | 78·3 |
| Formic acid N/50 | 35·3 | 50·0 | 34·0 |
| Oxalic acid N/50 | 38·1 | 51·7 | 41·6 |
| Sodium bisulphate N/50 | 92·6 | 88·0 | 94·5 |

*Condition of the Leather at Temperature 60°C.*—The leather immersed in the hydrochloric acid was completely disintegrated, shrinking to about one-third its original size, and

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becoming very dark colored, the leather being commercially useless, as will be readily judged by the pattern here shown. The leathers immersed in the other solutions were apparently, so far as one could judge without mechanical testing of tensile strength, quite uninjured, and certainly appeared to be good, sound commercially saleable leather.

At the temperature of 65°C. the leather treated with hydrochloric acid presented an appearance of having been burnt, being almost black in color, and on removal from the dye-bath presented a somewhat pelty appearance, and eventually dried hard, horny and brittle. The piece of leather treated with sulphuric acid also shrank in size, darkened somewhat in color, and the leather when dry was found to possess little fibre and be exceedingly hard and very brittle. The leather treated with oxalic acid and the sodium bisulphate did not shrink, but was somewhat tendered by the treatment, the grain being brittle, cracking easily on bending, but the pieces of leather did not possess the ruined, unsightly appearance of those just mentioned.

Contrary to expectations, the leather immersed in plain water at this temperature and the one treated with formic acid were not visibly affected, and when dry were apparently good, sound leathers.

Of the pieces of leather immersed at 70°C., all were detrimentally affected except the one treated with plain water, which apparently had suffered no very serious injury at this high temperature.

Pieces of leather were now immersed in (a) water, (b) oxalic acid (N/50), (c) formic acid (N/50), (d) sulphuric acid and sodium sulphate, at a temperature of 75°C., these reagents being selected because they had the least action at a temperature 70°C. In this case the whole of the samples showed considerable deterioration, but the one immersed in plain water presented much the better appearance by comparison.

From the foregoing experiments it is very obvious that leather will without serious injury stand immersion in plain water at a very much higher temperature than is possible when

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acid is used; and that formic acid possesses a much less injurious action than any other of the acids that have been tried in these experiments.—Leather Trades Review.

## REVIEWS

**The Investigation of Egg Yolk.** J. PAESSLER. *Gerber Zeitung.*, 1907, through Collegium, 1908, p. 56.—Schorlemmer and Sichling have earlier (Collegium, 1906, 90, 94) called attention to the different results obtained by them in the analysis of egg oil extracted from commercial egg yolk as compared with those obtained by Vignon and Meunier (1904, Collegium 325, 335) who extracted their material from eggs directly, first quantitatively separating the yolk after boiling and then extracting the fat with chloroform.

| Analysis of oil from | Vignon and Meunier | | Schorlemmer and Sichling | |
|---|---|---|---|---|
| | Hens' Egg Yolk | Ducks' Egg Yolk | Egg Yolk A | Egg Yolk B. |
| Iodine number ..... | 52 | 37 | 66.5 | 68.2 |
| Non-saponified, per cent. | 0.2 | 2.7 | 2.91 | 4.35 |
| Phosphoric acid, " " | 2.33 | 1.91 | 3.19 | 3.28 |

They attribute the discrepancies, especially in the amount of non-saponified matter to the presence of the large amounts of salt, etc., used as preservative in commercial egg yolk; also this always contains some of the white which on the chloroform extraction will certainly give up some soluble material affecting the result. They therefore propose that for such investigations eggs be employed directly and the separated yolk be subjected to the commercial preservative treatment and later to analysis.

The following results were obtained at the German Experiment Station for Leather Industry in pursuit of this plan. The eggs used were broken and the yolk superficially separated with some white still adhering. This was preserved with about 12 per cent. of salt and after several weeks standing the product was analyzed.

| | Hens' Eggs | Ducks' Eggs |
|---|---|---|
| Yolk, per cent..... | 33.7 | 39.6 |
| Yolk analysis: | | |
| Water, per cent..... | 45.9 | 46.9 |
| Oil, per cent..... | 29.6 | 29.8 |
| Egg Oil, analysis: | | |
| Iodine number..... | 45.9 | 54.2 |
| Unsaponified, per cent. ..... | 3.4 | 6.2 |
| Phosphoric acid, per cent. ..... | 3.7 | 3.1 |

These results agree fairly with those of Schorlemmer and Sichling obtained with commercial egg yolk aud confirm their views regarding the discrepant results of Vignon and Meunier. Paessler regards it as desirable, however, to extend these investigations, particularly with eggs from various sources in order to obtain reliable averages.

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**The International Method of Tannin Analysis.** U. J. THUAU. *La Halle aux Cuirs*, through Collegium, 1908, p. 82.—The new method of analysis originating in America and adopted in England has not been accepted by Germany since it could nourish only one of its industries without at all favoring another. The syndicate of German extract manufacturers demanded from the laboratories of the tanneries what were the differences furnished by the old and new methods. The conclusion was that in liquid extracts containing about 30 per cent. tannin, the content was lowered by one to three per cent. by the new method, and four to six per cent. in the solid extracts. The syndicate decided therefore to adhere to the old method.

In France both methods are employed, although the extract makers prefer the old. The writer, who represents a consulting analytical laboratory for leather industry in Paris has made a comparison of the two methods and determined a series of coefficients which may be used to convert the results obtained by one method into those by the other. While the approximation is not so close by using this computation instead of the direct analysis, the table may be considered useful to the practical tanner or extract maker.

| | NON-TANNINS. | | | |
|---|---|---|---|---|
| Extracts | Filter Method | Shake Method | Difference | Coefficient |
| Pure chestnut | 9.5 | 10.9 | 1.4 | 1.147 |
| Chestnut with myrabolams | 9.8 | 11.5 | 1.75 | 1.173 |
| Liquid myrabolams | 10.0 | 11.57 | 1.57 | 1.157 |
| Oak | 16.7 | 17.2 | 0.5 | 1.030 |
| Quebracho, solid, pure | 6.0 | 8.2 | 2.2 | 1.366 |
| Quebracho, liquid, decolorized, but not sulphited | 6.1 | 6.1 | 0 | 1.0 |
| Quebracho, liquid, sulphited (Mimosa D) | 11.0 | 13.4 | 2.4 | 1.218 |
| Tanning materials | | | | |
| Oak bark | 6.4 | 6.8 | 0.4 | 1.062 |
| Pine bark | 9.1 | 10.9 | 1.8 | 1.198 |
| Sicilian sumac | 14.5 | 15.8 | 1.3 | 1.087 |
| Myrabolams | 11.4 | 13.8 | 2.4 | 1.210 |

**Boiler Water and Its Purification in the Light of Physical-Chemical Theory.** A. AUFHAUSER. *Zeit. f. angew. Chem.*, 1908, through Collegium, 1908, p. 90.—It is beginning to be seen that this subject cannot be treated along purely chemical lines, particularly since physical conditions, above all pressure and temperature, prevail in practical operation.

We have in boiler water to consider the problem of chemical equilibrium dependent upon forces chiefly of physical nature and the distinct problem of equilibrium of solution, both being involved with each other.

Since the temperature and amount of water are constant, the maximum of solubility for each of the dissolved substances is fixed, but since the amount of these increase with continued feed, the equilibrium of solubility

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of each is approached with time, and soon passed for the less soluble with deposit of scale.

The ionic theory is important in the study of the changes in chemical equilibrium, the degree of electrolytic dissociation of the dissolved substances explaining the slow and imperfect reactions taking place. The conception of statical and dynamical moments was employed by the speaker in discussing the various agencies. Among the statical moments he emphasized that of the reaction between the salts and water itself, the hydrolysis yielding free acid causing great injury, especially when both magnesium salts and chlorides are present.

The physical-chemical theories also yield new deductions bearing on the purification of boiler water. The easily soluble ingredients deserve as much attention for their harmful action as the boiler scale formation which is often considered the specific feature of injury. If help is sought through preliminary purification of the water or by addition of material then the laboratory work of the chemist should be directed towards exact maintenance of the conditions of equilibrium pertaining in practical operation.

**The Employment of Sodium Hydrosulphite in Volumetric Analysis.** H. BOLLENBACH. *Chemiker-Zeitung*, (1908), 146, through Collegium, (1908), 75-6, 78-82, 86-7.—This salt, now to be obtained in solid form and high grade of purity, has proved useful to the analyst in many cases. O. Brunck has thoroughly studied its employment in gravimetric work; it is suited for precipitation of several metals and according to the writers investigation reduces chlorates, bromates and iodates in hot alkaline solution to chlorides, bromides and iodides, which can be precipitated in the usual way with silver nitrate.

Bernthsen employed the reagent for the volumetric determination of copper in ammoniacal solution, titrating to discharge of the blue color, producing cuprous salt; the reduction can go further, however, producing metal which obscures the end point. Bernthsen added indigo-blue and obtained better results. This method according to the writers' experience, is preferable to the cyanide method of Parkes, the sulphocyanide method of Volhard or the titration with thiosulphate after addition of potassium iodide.

Volumetric determination of iron.—The writer points out some of the disadvantages of the familiar titrations of iron, and claims that Knecht's superior method with titanium trichloride cannot compete with hydrosulphite, this being cheaper.

Brunck showed that ferric salts were instantaneously reduced in the cold with sodium hydrosulphite. Sulphur dioxide is evolved and frequently free sulphur, producing cloudiness, which can be avoided by vigorous stirring. After a renewed study of this reaction by the writer, he found that correct results could be obtained by using sufficient sulphuric acid to dissociate any ferric chloride present. The end-point of the titration is recognized by discharging the red color produced by adding potassium sulphocyanide as an indicator; this is made still sharper by addition of a drop of

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indigo solution. The bleaching of this by hydrosulphite resembles the iodine starch reaction. Experiments showed that it was not necessary to exclude air during the short time required for reaction.

Crystallized sodium hydrosulphite from the Badische Anilin u. Soda-Fabrik was used ; this is not fully pure but can be employed direct for titration, since the solution must always be first standardized before use. Several grams of the salt are placed in a half-litre bottle, moistened with a few cc. of conc. sodium carbonate solution ; the bottle is filled with water and thoroughly shaken. After settling, the clear solution is poured off and must be preserved with exclusion of air, best in an aspirator bottle placed above the burette which is connected for continuous supply, without admission of air. The top of the reservoir bottle communicates with a supply of carbonic acid, hydrogen or coal gas which is best freed entirely of oxygen by washing with a concentrated solution of hydrosulphite, which according to Franzen quantitatively absorbs oxygen.

For standardizing, both ferrous ammonium sulphate and ferric alum from Kahlbaum were used, analyzing pure by gravimetric control analysis, The ferric salt was used direct for titration, the ferrous salt was first oxidized with permanganate and boiled colorless after addition of a drop of alcohol. For titration, the iron solution was measured off into a beaker, acidified with sulphuric acid, and a drop of 10 per cent. potassium sulphocyanide added. A small amount of hydrosulphite was drawn from the burette and discarded and the tip then dipped one mm. in the iron solution and after reading, the hydrosulphite solution was run in until the red color was nearly discharged. Then one or two drops of indigo solution (of a strength about one-tenth the hydrosulphite) were added and titrations carefully continued until disappearance of the blue color. The indigo should not be added at the outset since large amounts of iron solution may bleach it by oxidation. Distilled water should be used which has been freed from air by boiling and quickly cooled. The standardization should be made soon before use in titration of an unknown iron solution and with nearly the same volumes of solution.

The temperature of a solution to be analyzed should not exceed 30°. Sufficient sulphuric acid must be added to discharge the yellow color of any ferric chloride as easily observed against a white ground. The titration is carried out as in the standardization. The discharged blue reappears soon from action of the air on indigo-white, but not so quickly as to interfere with titration. Organic substances like acetic and tartaric acids and glycerine, or metals of the ammonium sulphide group, cobalt, nickel, aluminum, zinc, manganese, chromium, do not interfere. Metals precipitated by hydrogen sulphide are likewise thrown down by the hydrosulphite and must first be removed by the former.

The method fails in the presence of hydrofluoric acid.

According to Bernthsen, the reaction of hydrosulphite with an ammoniacal cupric solution is

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$$Na_2S_2O_4 + O + H_2O = 2NaHSO_3.$$

In the above titration with iron, sulphur dioxide was evolved. The hydrosulphite solution standardized against a cupric solution gave the same factor with a standard ferric solution, proving the equation

$$Na_2S_2O_4 + Fe_2(SO_4)_3 + H_2SO_4 = 2FeSO_4 + 2NaHSO_4 + 2SO_2.$$

A series of titrations are quoted giving 99.6 to 100.3 per cent. of total iron used.

## PATENTS

**Manufacture of Leather Belting and Machinery Therefor, U. S. Patent No. 884,528,** to E. F. SARGEANT, STROUD, England. An improved method and machine for making leather belting.

**Preparation of Hides for the Manufacture of Leather, U. S. Patent No. 886,411,** to OTTO ROHM, Esslingen, Germany. A bating process consisting in treating the hides with an aqueous pancreatic extract containing a mixture of salts of alkali, and ammonia.

**Process of Black-Dyeing Chrome Leather, German Patent No. 189,468,** to W. EPSTEIN, Frankfort, Germany. The leather is treated with acidified solutions of bichromate or chromic acid, and of aniline salts. The chrome solution contains the necessary amount of chromium derivatives for dyeing and the aniline solution an excess of the aniline salt, so that there is sufficient to dye the leather and reduce the chromic acid.

**Machine for Treating Hides, Skins and Leather, U. S. Patent No. 887,121,** to F. J. PERKINS AND J. W. SMITH, Woburn, Mass. An improved hide and leather working machine.

**Feed Roll for Leather Skiving Machines, etc., U. S. Patent No. 887,625,** to R. P. GRANT, Boston, Mass. A feed roll, the face of which is formed by the perimeters of alternating rigid and elastic sections, the rigid sections being serrated to engage the material being fed, and the elastic sections adapted to be compressed by the material being fed,

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## THE 1908 I. A. L. T. C. CONVENTION.

The undersigned has received a letter from Prof. Dr. H. Becker, President of the I. A. L. T. C., announcing that the coming Convention of the I. A. L. T. C. is to be held at Brussels, Sept. 20 to 23rd inclusive and most cordially inviting the members of the A. L. C. A. to attend this Convention. It is to be hoped that as many members as may find it possible will avail themselves of this opportunity to meet personally our Colleagues across the sea.

F. H. SMALL, *President*, A. L. C. A.

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## NOTES AND OBSERVATIONS ON "COCKLE" IN SHEEP AND LAMBSKINS.

*By Alfred Seymour-Jones.*

Everyone who has the handling of sheep and lamb pelts is familiar with the curious eruption, which appears upon certain classes of sheep and lamp pelts, particularly in the spring of the year, known to the Anglo Saxons under the title of "Cockle." The origin of the word "cockle" as applied to this form of pelt deterioration would seem to be almost as mysterious as its name.

The word "Cockle" is evidently derived from its appearance to the wrinkles of a cockle-shell. It is used to denote unevenness,—*vide* Century Dictionary. "The sorting together of wools of several natures causeth cloth to cockle and lie uneven." Hakluyt's Voyages, II, 162. "Parchment does not cockle unless wet through."—Workshop Receipts, 2nd sec., p. 251. "Also, to rise into frequent ridges, as the waves of a chopping sea. A short cockling sea which must very soon have bulged the ship." —Cook's Voyages, I, III, 7.

Anyone who wishes to pursue this point further is recommended to refer to any up to date Encyclopedic Dictionary. Sufficient is it for the purpose of this article that the word "cockle" is applied to this form of sheepskin eruption, because of similarity to the cockling, wrinkling, or puckering of other articles like parchment, cloth, silks, etc.

The "cockle" or cockling of a sheep or lamb pelt is, as the sheep leather traders all know, a disturbance of the pelt structure, which may be said to resemble a hard pimple or boil of marked and definite appearance on the grain, ranging in regular waves or ridges from the spine outward, and commencing on the neck or shoulder, sometimes covering the whole skin, but more frequently ceasing with the ribs. In the beamhouse the "cockle" have a yellow to white appearance, and may be easily mistaken for gristle. They do not disappear during any of the leather manufacturing processes. After tanning they are particularly apparent, being of a red to a deep black red shade, according to the tannin employed, the center being darker than the surrounding. After shaving and subsequent processes they will either become more prominent, or may sink or appear thin-

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ner and harder than the unaffected parts. All leather dressers object to cockly skins and would be glad to be free from having to buy them.

For over twenty years I have made a close study of this cockle trouble, but have been loth to place my observations on paper until the cause appeared clearer to me. Although I have collected a mass of information upon the subject, I feel very considerable hesitation in placing it before agriculturalists, and all others interested in sheepskins, knowing how incomplete is the information I have to give, and that others have probably done greater work, but I do so in the hope that some interest may be awakened in observers to study, not only "cockle," but other pelt troubles, and to give the world the benefit of their observations, experience, and deductions.

The following remarks are not to be taken as conclusive, but suggestive: "Cockle" would appear to be indigenous only to those sheep which are grown particularly for their wool, and whose skins possess an amount of fat or grease, which is almost absent in the hair sheep. For example—European, Australian, New Zealand, southern portion of South America, northern portion of North America sheep are of the fleece-bearing and fatty-skin class, whereas Arabian, Indian, etc., sheep are hairier and free from fat, and *free from cockle* so far as I can learn. Nor have I heard of it appearing in goat-skins, nor even domestic bred and fed goats. "Cockle" commences to appear about December, and is at its worst immediately before shearing. It is accurate to say no spring of any year passes away without "cockle" appearing more or less. Some seasons it is very bad, while at other times it assumes only a mild form. Also it is curious but true, that every vestige of "cockle" disappears within a few days, say, 7 to 10 days after shearing.

To test the accuracy of certain views and opinions formed, about twenty years ago I prevailed upon a large sheep owner to permit experiments to be made upon a number of his Shropshire breed of sheep—they were a prize breed and calculated to yield "cockle" in superabundance. Fifteen sheep were taken in November 1888, divided them into three lots of five each; all fifteen were out to grass until clip, but the extra or fattening food was varied.

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Lot 1 were extra fed on oilcake and dry foods.
Lot 2 were extra fed on oilcake alternated with roots.
Lot 3 were extra fed on roots and moist food only.

When clip time came round, the right hand side, or half, of each animal was shorn, leaving the other or left half with the fleece intact. Three days afterwards they were slaughtered, and subsequently the skins were depilated with ordinary lime paste. An examination of the pelts showed that all fifteen skins were cockled on the left or unshorn side in the following order: No. 1 Lot in its worst form, No. 2 bad, No. 3 moderate. The right or shorn side of No. 1 bore the appearance of having been badly cockled, but was rapidly disappearing or healing. No. 2 the remains of "cockle" was slightly apparent. No. 3 the appearance of where "cockle" had been could only be observed in one skin.

The conclusions drawn were that dry food produces not only more, but harder "cockle" and in its worst form, while moist cooling and opening foods were conducive to milder "cockle" with probable decrease. Following up this experiment by observation over years, I noted that open winters, with plenty of good grass and root crops for food made for reduced "cockle," but when farmers had to fall back upon artificial foods, oilcake, etc., the "cockle" appeared in its worst form. So far, so good, but why does "cockle" disappear a few days after clip?, especially when the same food would be given to the sheep probably four to eight week afterwards. It was observed that invariably the more cockly the skin, the less grease the skin appeared to contain, although it might contain hard fats. I wish to make it quite clear what is meant by grease and fat—by grease, I mean, that which may be fully wrung out in a wringer, or expressed by hydraulic pressure in the leather factory, but not the harder fats or lime soaps, which can only be removed by naphtha, or a similar solvent.

If the statement is correct that "cockle" exists only in wool sheep possessing greasy pelts, and that the greasier the pelt the more bountiful the wool; further, that cockled skins are singularly devoid of grease, then as winter approaches nature claims her right to increase the sheeps coat of wool, the fattening of the sheep does not proceed at the same rate as before, but the wool

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commences to increase in body and bulk; in doing so, it exhausts the wool-fat or grease from the pelt or skin, the heat of the skin is increased bringing the grease and fat into greater liquidity in order that it may filter out more freely and into the wool, undergoing probably during the process some chemical change. While this draft is being made by the wool upon the skin for its fat a process of fineing is going on within the skin; the harder waxes (probably one of the Cholestrol group) are left behind in the pelt, grouping together into lines or waves of least resistance, and form what are termed heat lumps or "cockle." A chemical analysis will prove that "cockle" are largely composed of alcoholic fats, of one or more of the cholestrol group. A confirmation of this theory is the rapid restoration of the skin to its normal condition free from "cockle" plus a large quantity of greasy fat in a few days after being freed of its fleece.

A short time ago while conversing upon "cockle" with a friend who is connected with, probably the largest freezing company in New Zealand, he informed me that in New Zealand, when grass crops failed, or at certain seasons of the year, the farmers turned the sheep on to "rape" feed, but they had to exercise care, because of its great feeding and heating properties, so much so, unless watched, the overheating so affected the ears, as to make them diseased, and eventually drop off; and in his experience such skins were always cockly.

This "rape" is probably the same plant from which the rape-seed oil, and rape-seed cake, is extracted for feeding European sheep in winter, because of its fattening qualities.

There is one interesting feature about "cockle:" leather dressers experience frequently, lambs which have every appearance of having been born with "cockle," this is probably due to the feed of the ewes, but I am not aware of "cockle" appearing in lambskins after the lambs have been able to forage for themselves.

To sum up,—"Cockle" is evidently unavoidable in wool sheep, but agriculturalists may do much to reduce its virulence, by giving the sheep moist food during winter and early spring.

Leather manufacturers up to now have no known method by which to remove the hard fatty waxes which play an important part in forming the "cockle." Supposing they had, the dis-

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turbed portion of the pelt "cockled" would still remain a blemish.

For "Cockle" there appears no remedy, except to permit nature to restore the skin to its healthy condition, after the heavy wool drain has been clipped or shorn away.

If any reader has thoughts or observations on "cockle" I trust he will either publish them, or write me with permission for publication at some future time.

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## "DRY DYEING."

An interesting paper was recently read before the London section of the Society of Dyers and Colourists entitled "Dry Dyeing," by Messrs. F. J. Farrell, M. Sc., and C. W. May. The process can be employed in the dyeing of leather, furs, etc., and in many cases shows an improvement on the wet method at present employed. Especially is this the case with made-up articles such as bags, belts, gloves, shoes, etc., which cannot be satisfactorily dyed in the ordinary way. The term "dry" is employed to signify that the articles are not wetted in the ordinary sense of the term; that is to say, an article immersed in or stained with petroleum benzine does not alter in shape or color.

As suitable media for dry dyeing, we are practically limited to petroleum benzine and benzol, or analogous neutral substances such as chloroform, ether, carbon tetrachloride, toluol and other homologues of benzol. Ether is excluded by its low boiling point, and chloroform by its toxic properties and cost, while toluol, zylol, etc., possess no advantage over the less expensive benzol. Carbon tetrachloride finds a limited application because of its noninflammability, and if the cost of production could be reduced would compete seriously with benzine and benzol.

Basic coloring matters, which, as hydrochlorides, are practically insoluble in benzine, may be rendered readily soluble by conversion into oleates, stearates, or resinates. The colors produced ("fat colors") have been employed for several years in dry dyeing, coloring waxes, etc.

The usual method of preparation of "fat colors" is to dissolve the basic color in water, adding the solution obtained to an aqueous solution of a tallow or oil soap (or the color and

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soap may be dissolved together); when the mixture is cold, hydrochloric acid is added. This precipitates a mixture of fatty acid and "fat color," which latter rises to the surface, and may be collected, washed, and dried. The drying is performed by melting and separating from any contained water by cooling and removing the fat layer.

The following quantities may be taken as an example:— Dissolve in 100 parts of hot water 1 1-4 parts methyl violet, 5 parts curd or white oil soap; when cold add 2 1-2 parts concentrated hydrochloric acid. The resinates are prepared in a similar manner, after previously dissolving the resin in a solution of caustic soda. The coloring matters prepared by either of these methods are dissolved in benzol or benzine, and the previously cleaned goods can be dyed by immersion or brushing.

After dyeing it is very difficult to remove the superfluous color solution without obtaining patchy results. The authors find that more satisfactory results can be obtained by the addition to the bath of considerable quantities of benzine soap or oleic acid (from 5 to 10 per cent.).

The soap employed was Grünwald and Stommel's Saponine, which is prepared according to the patent specification by melting together equal quantities of soap and oleic acid until a clear liquid is obtained. A 10 per cent. solution of Saponine in benzine will dissolve direct all basic dyestuffs in sufficient quantities to yield solutions giving medium and in most cases dark shades. The authors also found that a 10 per cent. solution of Saponine in benzine will remove basic dyestuffs from fibres, whether dyed direct or on a tannin mordant. The results not being satisfactory with the basic colors, a series of experiments were conducted with the "acid" dyestuffs, as many of this class of colors are freely soluble in alcohol, particularly the sulphonated triphenylmethane colors. Absolute alcohol is miscible in all proportions with benzine and benzol, whilst methylated spirit (which contains about 10 per cent. water) is not, but can be rendered soluble by the addition of Saponine.

By experiment it was found that benzine is not miscible in equal volumes with alcohol containing more than 6 per cent. water, whilst a very slight increase in the percentage of water

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causes the almost complete separation of the benzine. Twenty-five per cent. of Saponine in benzine mixes in all proportions with methylated spirit, and 3 per cent. of Saponine in benzol is also miscible in all proportions, whilst carbon tetrachloride containing 4 per cent. of Saponine, is miscible in all proportions with methylated spirit. Trials were also made with anhydrous potassium oleate, and the results differed slightly from those obtained with Saponine, the volume of methylated spirit which its solutions would dissolve being increased, due to the fact that Saponine contains an appreciable percentage of water. It was found that the solubility of alcohol in solutions of benzine soap in benzine depends to a very large extent upon the amount of water in solution in the alcohol, a variation of 1 per cent. making the difference between solubility in all proportions and solubility to the extent of 20 per cent. only, likewise for a given percentage of water the quantity of alcohol soluble in benzine depends upon the amount of benzine soap in solution.

The following acid colors were found to be the most soluble in methylated spirit:—

Acid green, extra conc.
Acid magenta.
Acid violet, 10 B.
Azo rubine, A.
Croceine scarlet, B and 3 B.
Cyanole, extra.
Fast acid violet, A 2R.
Indian yellow, G. and R.
Orange II.

Also:—

Eosine, extra.
Patent blue, A.
Phloxines.
Rhodamine, B.

The solutions of these dyestuffs in methylated spirit must in all cases be filtered and as strong a solution as possible is made without being saturated. The best results for dyeing were obtained by taking 10 cubic centimeters of alcoholic dye solution and 290 cubic centimeters of benzine containing 10 grams of Saponine. An equal depth of color is obtained

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by employing anhydrous potassium oleate and oleic acid plus 6 per cent. of water, and by the addition of further quantities of water darker shades can be produced, but not more than 10 per cent. of water on the weight of the potassium oleate, and not less than 6 per cent. can be employed without separation occurring. After dyeing, the fabrics may be rinsed in benzine, and after the removal of the superficial color and adhering dye solution, no further color is removed by rinsing in clean benzine. In practice it is better to err on the side of employing too much rather than too little of benzine soap, so as to minimize the risk of separation occurring. The filtered dyestuff solution is dissolved in several times its volume of a 25 per cent. solution of Saponine in benzine with constant stirring, and diluted to the requisite strength by the addition of a 10 per cent. solution of benzine soap. The quantity of dyestuff should be such that the shade required is produced by at least half an hour's immersion. The articles for dry dyeing must be well cleaned with benzine soap, and can then be placed in the dye bath straight away, or they can first be dried after cleaning.

Acid colors, unlike the basics, are quite fast to a cold 10 per cent. solution of benzine soap.

Good results were obtained by the authors on greasy Persian sheep, both by immersion and brushing, but they were not so successful upon fat-liquored chrome sheep.

At the close of the meeting, in reply to a question by one of the members, Mr. Farrell stated that if an acid dyestuff was fast in any particular way in ordinary dyeing it would be equally fast when dry dyed.—Leather Trades Review.

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## THE COMPOUNDS OF GELATIN AND TANNIN.[1]

*By J. T. Wood.*

On February 4, 1803, a paper was read before the Royal Society entitled "An account of some experiments and observations on the constituent parts of certain astringent vegetables, and their operation in tanning," by Humphrey Davy, Professor of Chemistry in the Royal Institution (Phil. Trans., 1803, 233).

[1] Read before the Nottingham Section of the Society of Chemical Industry.

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In this paper, so far as I know, the first account is given of the compound formed when gelatin is added to solutions containing tannin. I had occasion to refer to this paper for information about these compounds in attempting to answer the question "what are the combining proportions of these two bodies?" I sought for this information with the object of throwing some light on the combining proportions of skin and tannin, for, on making some preliminary experiments with gelatin, it was evident that there was no definite combining proportion in a chemical sense, but that the proportions varied according to the concentration of the solutions, the amount of each of the bodies present, and possibly according to the rate at which the precipitate is formed and the temperature. I found Davy's paper most interesting as one of the earliest scientific contributions to the chemistry of tanning. He makes the following remarks:—

"The tanning principle in different vegetables, as will be seen hereafter, demands for its saturation different proportions of gelatin, and the quantity of the precipitate obtained by filtration, is not always exactly proportional to the quantities of tannin and gelatin in solution, but is influenced by the degree of their concentration. Thus, I found that 10 grains of dry isinglass, dissolved in two ounces of distilled water, gave with solution of galls in excess, a precipitate weighing, when dry, 17 grains, whilst the same quantity dissolved in six ounces of water produced, all other circumstances being similar, not quite 15 grains. With more diluted solutions, the loss was still greater; and analogous effects took place when equal portions of the same solution of isinglass were acted upon by equal portions of the same infusion of galls diluted in different degrees with water, the least quantity of precipitate being always produced by the least concentrated liquor. In all cases, when the weak solutions were used, it was observed that the residual fluid though passed two or three times through the filter, still remained more or less turbid and opaque, so that it is most likely that the deficiency arose from the continued suspension of some of the minutely divided solid matter in the liquid mass."

The standard solution of gelatin which Davy used for making his experiments, was made by dissolving 120 grains of isinglass in 20 ounces of water (this is equivalent to 13.7 grams per

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liter), the temperature at which the precipitation was made being between 60° and 70° F. Great care was taken to prevent the presence of any excess of gelatin, as Davy found that when this excess exists, a portion of the precipitate is re-dissolved. The precipitate was filtered off and dried upon the lower plate of a sand bath at a temperature not exceeding 150°F.; the isinglass used was dried in the same manner in order to eliminate the effect of moisture. He does not say if he washed the precipitate, but from the results given I am inclined to think that he did. As a result of his observations he concluded that 100 grains of the compound of gelatin and tannin, formed by precipitation from saturated solutions, contain about 54 grains of gelatin and 46 of tannin; this is equivalent to a precipitation of 85 parts of tannin by 100 parts of gelatin. According to Lipowitz (Jahresb. Forts. Chemie, 1861, p. 624) 100 parts of isinglass dried over sulphuric acid precipitates exactly 65 parts of tannin. In the determination of gelatin by the Bisler Beumat method (Rideal, Glue & Glue Testing, 1900, p. 111), 42.7 parts of gelatin are said to be equivalent to 57.3 parts of tannin, or 100 parts gelatin precipitate 134 parts of tannin. According to Mulder (Allen, Comm. Org. Anal, IV, p. 463) 100 parts of dry gelatin precipitate 135 parts of gallotannic acid. R. Williams (Allen, p. 484) by precipitating 1 per cent. solutions of glue with pure tannic acid, and estimating the excess of tannin by Lowenthal's process, found 77.5, 77.9 and 78.6 parts of tannin precipitated by 100 parts of glue or gelatin. Procter (Principles, p. 63) quotes Böttinger, who by Kjeldahl's method found the precipitate produced by adding gelatin to excess of gallotannic acid to contain 66 per cent. of gelatin, which is equivalent to 50 parts only of tannin precipitated by 100 parts of gelatin. It is difficult to explain the great divergence between the maximum and minimum amounts of tannin precipitated, though the figures appear to resolve themselves into two groups, in one of which the tannin is from 66 to 85, in the other about 135 per 100 parts of gelatin.

It seemed possible to investigate this matter in a similar way to that employed in the investigation of the combining proportions of skin and tannin, (see note on the absorptive properties of chromed skin for tannin, Collegium, No. 222, Sept. 1, 1906,

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301. J. S. C I., 1906, 896). I used Coignet's Gold Label gelatin, the same as described in a "Note on Collin." (Wood & Trotman, J. S. C. I., 1904, p. 1071), and which by Kjeldahl's method, using the factor N×5.5, contained 74 per cent. of gelatin, and by precipitation with zinc sulphate was found to contain 1.78 per cent. of nitrogenous matter not gelatin. For most of the experiments a 2 per cent. solution of this gelatin was used. The method employed consisted in adding 50 cubic centimeters of gelatin solution containing one gram of air dry gelatin to the tannin solution, shaking well; allowing to stand for varying lengths of time, filtering through S. & S. 605 filter and evaporating a sufficient quantity of the filtrate to give from 0.3 to 0.6 grams of residue, from the weight of the residue the quantity of tannin precipitated was calculated. The residues contained only traces of nitrogen, as shown by Kjeldahl's method, due to the small quantity of nitrogenous matter above mentioned which was not precipitated by the tannin, the maximum amount of this nitrogen, if calculated as gelatin, was 0.014 grams per 100 cubic centimeters. The tannin used in some of the experiments was Hasting's tannin containing 95 per cent. by hide powder (*see* Collegium, 1906, 302), and later Kahlbaum's pure tannic acid containing 96.5 per cent. by hide powder and 100 per cent. by Lowenthal on the dry matter.

A few preliminary experiments showed that the quantity of tannin precipitated by this gelatin, when a large excess of tannin was employed, was greater than that found by Davy, and on repeating the experiments with isinglass instead of gelatin similar results were obtained. I found that the greatest amount of tannin which could be precipitated by 1 gram of air dry gelatin was about 2.4 grams from a solution containing 6 grams of tannin, the volume of the solution after the addition of gelatin being 150 cubic centimeters.

It was found from these experiments that to obtain the maximum precipitation a large excess of tannin was necessary, about six times the weight of gelatin used. Unless this large excess of tannin be present the gelatin does not carry down so much tannin as it is capable of doing. I believe that all experimentists, including Davy, got erroneous results because they thought that if tannin were present after the addition of the gelatin, they

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had an excess of tannin over and above what would combine with the gelatin, whereas I have found that unless a definite excess is present the maximum amount of tannin is not precipitated. The results obtained are shown in the following table:—

*Amount of tannin precipitated by 1 gram of air dry gelatin in solutions of equal concentration but different volumes.*

| Tannin, grms. | Volume of solution, cc. | Tannin precipitated, grms. |
|---|---|---|
| 1 | 100 | 0.91 |
| 2 | 200 | 1.50 |
| 3 | 300 | 1.90 |
| 4 | 400 | 2.17 |
| 5 | 500 | 2.28 |
| 6 | 600 | 2.36 |
| 7 | 700 | 2.36 |
| 8 | 800 | 2.36 |

It has been known that the precipitate of gelatin with excess of tannin was of different composition to the precipitate with excess of gelatin, and that by washing the former with hot water a considerable amount of tannin could be removed from it, but I have not been able to find any record of experiments made with definite quantities of tannin and gelatin. In order to ascertain how much tannin could be washed out I made use of Kjeldahl's method; the precipitate after filtering off the tannin was transferred to a beaker and washed by decantation with five lots of cold water; the wash water still gave a precipitate with a drop of 1 per cent. gelatin and a blue black coloration with iron alum. It was then washed with boiling water until the wash water gave no precipitate with gelatin and only a very faint coloration with iron alum. The nitrogen found in the dried precipitate before washing was 4.54 per cent., and 5.79 per cent. after washing, an increase of 1.25 per cent. equivalent to 6.9 per cent. of dry gelatin or 9.2 per cent. of original gelatin used

The composition of the precipitates on the dry matter was therefore:—

| | Unwashed. | Washed. |
|---|---|---|
| Gelatin | 25 | 32 |
| Tannin | 75 | 68 |

or for 100 parts of absolutely dry gelatin as estimated by Kjeldahl's method (5.5 factor), the tannin combined was:—Unwashed, 300; washed, 212. The amount fixed when calculated on the original gelatin used is 136 parts of tannin per 100 parts of gelatin, but if this amount of tannin be mixed in solution

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with the amount of gelatin indicated, the whole of the tannin is not precipitated, but an equilibrium is reached when about 87 per cent. of the tannin is precipitated. Two experiments gave the following results:—1.468 grams of Kahlbaum's pure tannic acid (=1.36 grams of absolutely dry acid) was dissolved in 50 cubic centimeters of water; to this was added 1 gram of Coignet's gelatin dissolved in 50 cubic centimeters of water; the whole was thoroughly stirred and allowed to stand 24 hours. After filtering and evaporating the filtrate as described, the amount of residue obtained in two experiments was 0.084 and 0.087 gram, equivalent to 1.192 and 1.186 grams of tannin precipitated, a mean of 1.189 grams, or 87 per cent. of the tannin was precipitated. On the gelatin as estimated by Kjeldahl, 1 gram precipitated 1.6 grams of tannin. If the quantity of tannin be successively increased, the gelatin and the concentration remaining constant, an increased quantity of tannin will be precipitated until the maximum above named, namely, 2.4 grams, or 3.25 N×5.5 is reached.

In order to ascertain the effect of time on the amount precipitated, experiments were carried out in which the filtrate was examined after the lapse of one hour, twenty-four hours, and forty-eight hours, the results being shown in the table below. They indicate that both for strong and weak solutions an equilibrium is reached in twenty-four hours, after which the precipitate appears to lose a little tannin. The table also shows influence of concentration on the quantity precipitated. One gram of air dry gelatin was used in each experiment and 6.04 grams of dry tannin.

| Experiment. | Time. | Volume of solution. | Residues. | Tannin precipitated by 1 grm. gelatin N × 5.5 | Concentration at beginning of experiment. | Concentration at end of experiment. % |
|---|---|---|---|---|---|---|
| | hours. | cc. | 25 cc. | | | |
| 1 | 1 | 150 | 0.6215<br>0.6225 | 3.10 | 4 | 2.45 |
| 2 | 24 | 150 | 0.6010<br>0.6000 | 3.25 | 4 | 2.37 |
| 3 | 48 | 150 | 0.6105<br>0.6100 | 3.15 | 4 | 2.4 |
| | | | 100 cc. | | | |
| 4 | 1 | 600 | 0.7545<br>0.7540 | 2.04 | 1 | 0.69 |
| 5 | 24 | 600 | 0.6665<br>0.6655 | 2.73 | 1 | 0.62 |
| 6 | 48 | 600 | 0.6690<br>0.6650 | 2.70 | 1 | 0.62 |

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The filtrate titrated with permanganate by Lowenthal's method was found to contain the same amount of tannin as that found by weighing.

In order to ascertain the influence of concentration on the amount of tannin precipitated, 1 gram of air dry gelatin (=0.74 gram by Kjeldahl's method) was brought into admixture with 5.51 grams of absolutely dry tannin under the same condition as above. The results are shown in the following table. These confirm Davy's results, and show that the least quantity of tannin is precipitated from the least concentrated solution.[1]

*Amount of Kahlbaum's gallotannic acid precipitated by 1 grm. of absolutely dry gelatin* N x 5.5 *in solutions of different concentration.*

| No. | Quantity of dry tannin. | Volume of solution | Concentration at end of experiment. | Tannin precipitated by 1 grm. of gelatin, N × 5.5. |
|---|---|---|---|---|
| | grams. | cc. | per 100 cc. | |
| 1 | 5.5 | 150 | 2.2 | 3.0 |
| 2 | 5.5 | 200 | 1.80 | 2.95 |
| 3 | 5.5 | 250 | 1.32 | 2.6 |
| 4 | 6.0 | 500 | 0.76 | 2.45 |
| 5 | 5.5 | 2000 | 0.19 | 2.4 |
| 6 | 5.5 | 6000 | 0.063 | 2.4 |

An experiment to show the influence of temperature was made by adding 1 grm. of air-dry gelatin to 1000 cc. of the tannin solution at a temperature of 80° C., an exactly similar solution being acted upon at 18° C., the amount precipitated in the former case being 1.74 grms., and in the latter, 1.35 grms. of tannin. In the hot solution the precipitate adheres to the rods and the sides of the beaker, and occupies a very small volume in comparison with the original precipitate.

The compound of gelatin and tanning when dry is a brittle mass of a yellowish brown color. When placed in boiling water it melts to a tenacious sticky substance of the consistency of bird lime, and in this state may be drawn out or spun into fibres

[1] Alsop (This Journal, 1907, 2, 405) shows that the same amount of hide powder in equal volumes of solutions of different density will give the same amount of non-tans. He infers this to be due to physical and chemical reasons and to be dependent on the volumes and not on the tannin content of the solution, but does it not rather point to a chemical combination, since the hide had absorbed the same amount of tannin from the strong as from the weak solution?

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as fine as those of a spider's web. The fibres have a metallic luster like silver slightly tinged with gold. When placed in a solution of iron alum they are but slightly colored blue, becoming the color of polished steel. The tannin in the compound is insoluble in alcohol, ether, or acetone, and is almost tasteless. I have been unable to observe any evolution or absorption of heat taking place during the precipitation. By boiling the pure preparations continuously with water they are decomposed into constituents of varying composition as shown by the appearance of the water; it contains tannin, and also fine suspended particles which may be filtered off and which appear to be another compound of tannin and a gelatin proteoid containing a much smaller quantity of tannin. By boiling with magnesia it appears to be completely decomposed. Approximately 1 grm. of dry gelatin (N x 5.5) combines with two grms. of dry gallotannic acid to form 3 grms. of "leather," but this compound can be partially split up by boiling with water, so that the compounds prepared by drawing the gelatin-tannin precipitate out of boiling water are not of constant composition.

Lumière and Seyewetz (Coll., 1906, 205; J. S. C. I., 1906, 704) state that tannin and gallic acid only produce the insolubilization of gelatin in the presence of air and in an alkaline medium; in the case of gallic acid this is true, and the observation is a very interesting one from the point of view of the theory of tanning, since alkaline gallic acid gives no precipitate with gelatin, but in the case of tannin I have not been able to confirm M. Lumière's observation; indeed, the tannin appears to act more vigorously in acid solution, and the same compound is formed as I have described above, which is insoluble in boiling water, although it is gradually decomposed by it. I think that what Lumière and Seyewetz have taken for the solution of the precipitate of tannin and gelatin on boiling, is its condensation or coagulation, for a very large volume of the precipitate is reduced to an extremely small volume by boiling, and if the experiment is carried out on a small scale is apt to be overlooked or neglected; it certainly appears as though almost the whole of the precipitate dissolved, but neither in the cold or hot solutions can I find any nitrogen or only a mere trace which may be accounted for by the presence of a small amount of nitrogenous

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matter in the original gelatin which is not precipitable by tannin. Unless the experiment is carried out quantitatively it is very easy to be deceived. The boiling of the solution causes the precipitate to part with a considerable amount of tannin (about 14 per cent. on the dry matter).

It is possible that the oxygen of the air has some influence on the fixation of tannin in the compounds I have shown, but I have been unable to make further experiments in this direction, though from what has been said above it will be seen that there is some fallacy in Lumière and Seyewetz's results.[1]

In view of the use of chromed hide in the estimate of tannin, I thought it of interest to ascertain the absorption of tannin by chromed gelatin. Lumière and Seyewetz (Bull. Soc. Chim., 1903, 1077; J. S. C. I., 1903, 1358) state that gelatin fixes a maximum constant quantity of sesquioxide of chromium of between 3.2 and 3.5 grms. per 100 grms. of gelatin, whatever be the chromium salt employed. I have been unable to confirm this, but find that the quantity of chrome fixed by the gelatin depends on the concentration of the chrome solution, and on the basicity of the salt used. By employing the basic chromic chloride as recommended for the chroming of hide powder (Coll., 1907, 252) sheets of gelatin placed for 24 hours in a solution diluted one-tenth gave 5 per cent. of chromic oxide, but when soaked in the concentrated solution 13.6 per cent. was found after washing and neutralizing in the same way as in the chrome tanning of skins, or, as recommended by Lumière and Seyewetz with weak ammonia. The gelatin is rendered absolutely insoluble even by the weaker solution.

The chroming of the gelatin does not interfere with the absorption of tannin, as a sheet of the heavily chromed gelatin will absorb as much tannin as before chroming. When a sheet of gelatin is soaked in cold distilled water it absorbs from 8 to 9 times its weight of water and loses about 5 per cent. of

[1] Since the reading of the paper Stiasny, Kritische und experimentelle Beiträge zur Aufklärung der Gerbevorgänge, Coll., 1908, 119, has shown that oxidation of hide fibre produces no alteration in its acid or basic characters, and consequently if leather be considered as a salt, that both oxidized and unoxidized hide are equally capable of forming it. Since gelatin is hydrolyzed hide fibre it is probable that the same holds good in this case too.

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soluble matter, the greater part of which is precipitable by tannin. This soluble matter is doubtless gelatin partially peptonized during the drying process. Such a sheet of swollen gelatin placed in a solution of tannin will absorb the tannin very much in the same way as a skin does, becoming tanned by the process, but the amount of tannin absorbed is not so great as that precipitated by the gelatin when in solution. A sheet tanned this way was found to have absorbed 1.06 grms. of tannin for every grm. of dry gelatin. An exactly similar sheet was chromed by treating it with a strong solution of basic chromium chloride as above described, and then transferred to a solution of tannin containing 5.5 grms. tannin for 48 hours. The amount of tannin absorbed (by difference) was 1.06 grms. per grm. of dry gelatin. Thus the chromed gelatin has absorbed as much tannin as the unchromed gelatin. From this it will be seen that the tannin attaches itself to different bonds in the gelatin molecule to those to which the chromic oxide is attached. Procter remarks on this—that recent researches on the proteids lead to the view that gelatin like the rest of them consists of linked chains of amino acids in which the carboxyl of one member is linked to an amino group of another, probably one or more carboxyls and one or more amino groups being free. It is therefore probable that bodies of an acid character attach themselves to the amino groups and those of a basic to the carboxyls, so that one does not interfere with the fixation of the other. There are many illustrations of the fact that this is so, such as the difficulty of attaching basic colors to chrome leather directly, etc., but whether the chemical explanation is the correct one is an open question which cannot be completely answered until we have carried investigations further as to the influence of the colloid state. In this connection I would cite an important paper by Lüppo-Cramer (Collegium, 1908, 24, Ueber einige Kolloiden Oxyde als Gerbungsmittel. J. S. C. I. 1908, 37), in which the mode of action of metallic oxides is shown to be due to their assuming the colloidal state; metals like silver, mercury, and copper, which will not tan in ordinary solution are capable of a tanning action when in the colloidal state. Some time back Dr. Sand suggested this possibility to

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me in the case of tin, but I have been unable to carry out any experiments for lack of time.

An examination of the facts shows that the combination of gelatin and tannin is neither a purely chemical one, since the gelatin and tannin compound is not of constant composition, nor a purely physical one, since it does not obey the solution laws, which require the concentration of the tannin in the solution and the tannin in the gelatin to maintain a constant ratio. The way in which the tannin combines with the gelatin very much resembles the combination of gelatin with hydrochloric acid (see Procter, Principles, p. 86). It is probable that more than one compound of gelatin and tannin exists, and that in the earlier stages only certain of the linkages are saturated with tannin. The whole matter is complicated for the reason that we know very little of the constitution of tannin and less of the constitution of gelatin. The investigations which are at present going on in various photographic and other laboratories are all tending to show that the influence of the colloid state is most important, and it is in this direction to which we must look for a fuller explanation of the various gelatin compounds of which the tanno-gelatin is the most important.

As to the explanation of the above facts, if I may be allowed to use the words of Newton "Hypotheses non fingo," I will merely content myself with adding them to what has been done already by others.

In conclusion my thanks are due to Mr. S. R. Trotman and Mr. W. E. Holmes for carrying out some of the experiments, and also to Professor H. R. Procter for his friendly advice and criticism.

DISCUSSION

Mr. O. Quibell remarked that he had found chondrin to be a frequent constituent of the gelatin referred to by Mr. Wood. This was to be expected from the process of the manufacture. He thought the term pure gelatin was somewhat contradictory.

Mr. S. R. Trotman thought that Mr. Wood's experiments were important from a practical point of view, since they indicated the proper excess of tannic acid necessary to obtain the maximum weight of leather from a given weight of skins. Interesting information might be obtained by a process of frac-

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tional precipitation of gelatin with tannic acid, and analysis of the resulting compounds. He had recently attempted to fractionally precipitate gelatin with magnesium or zinc sulphate. and the results of these experiments certainly confirmed the view that even the best commercial article was not a simple substance.

Dr. F. S. KIPPING also regarded the assumption that gelatin was a single substance as unwarranted, and suggested the use of amino-acids as precipitants, as it was possible that they played an important part in the constitution of gelatin. It would be interesting to know if the residues left by washing the gelatin tannate precipitation had been analyzed, and if so, whether they were of identical composition.

Mr. S. J. PENTECOST alluded to the capacity for absorbing tannic acid possessed by silk and the increased effect caused by subsequent treatment with metallic salts. This was perhaps similar to the reaction observed between chromed gelatin and tannic acid.

Dr. H. J. S. SAND thought that experiments such as those carried out by Mr. Wood were likely to throw light on processes occurring in some dyeing operations. With regard to Kipping's suggestion he thought that if gelatin were to be replaced by a pure amino-acid this acid ought to be a colloid. It was, however, doubtful whether a chemically pure colloidal amino-acid could be obtained.

Mr. WOOD in reply to Mr. Quibell, said that the gelatin he had used was remarkably constant in composition, samples analyzed during two years showing almost exactly the same nitrogen content and only a trace of nitrogen not precipitated by tannin. He had reckoned all the substance precipitated by tannin as "pure" gelatin, whatever that might be. He thought Mr. Trotman's suggestion a good one, but had not had time to carry it out. In reply to Dr. Kipping, he had already thought of the use of a pure synthetic protein, in fact he had himself suggested the use of such a body (J. S. C. I., 1904, 1072). Some time ago he wrote to Professor Sorensen of Copenhagen on the subject, who replied that to his knowledge no simple amino-acid, nor even the higher members nor the simple polypeptides are precipitated by tannin. The latter part of Pro-

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fessor Kipping's question he had answered in the paper, though perhaps he had not made it quite clear; was impossible to wash the residues to a constant composition with water since this decomposed the compound. If the excess of tannin he had indicated were present then he believed that the tannin actually combined with the gelatin was constant. In reply to Mr. Pentecost, Vignon of Lyon had proposed the use of raw silk as an absorbent of tannin in place of hide powder. He did not know whether the increased weight of the silk in the process mentioned by Mr. Pentecost was due to the tannin absorbed or to the metallic salts. In reply to Dr. Sand, he had compared the absorption of tannin to the dyeing process but the formula given by Biltz (J. S. C. I., 1905, 920) for the absorption of dyes, did not hold good for the absorption of tannin by gelatin. He hoped someone would be able to utilize the facts to which he had called attention.—Journal Soc. Chem. Industry.

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## ACID IN LEATHER DYEING: ITS ABSORPTION AND EFFECT.

*By M. C. Lamb, F. C. S., and J. W. Lamb.*

PART II.

The strength of acid used being greater than is present in the ordinary dye-bath employed when dyeing with acid colors, is was thought well to conduct a further series of experiments upon the same leather, using the same acids as previously employed, but half the strength used in previous experiments—*i. e.*, N/100. These experiments gave the following results:—

TEMPERATURE:—60°C.

| Treatment. | Number of cc. N/10 acid remaining in bath. | Number of cc. N/10 acid taken up by leather. |
|---|---|---|
| Sulphuric acid N/100..... | 3.4 | 75.6 |
| Hydrochloric acid N/100 .. | 6.9 | 73.1 |
| Formic acid N/100 ..... | 49.0 | 37.0 |
| Oxalic acid N/100..... | 32.0 | 39.3 |
| Sodium bisulphate N/100.. | ... | 83.3 |

It will be obvious that with the exception of formic and oxalic acids nearly the whole of the acid has been absorbed by the leather.

The foregoing experiments were, as previously mentioned, all conducted on calf that had been tanned with oak bark. It

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being well known that a leather well tanned by the older fashioned system of tanning with oak bark over a period of many months would stand immersion at a much higher temperature without apparent serious injury to the leather than a leather that had been quickly tanned, it was thought advisable to repeat some of the foregoing experiments upon leather tanned with other tannages. The leathers selected, particulars of which are given below, were sumach tanned skivers, sumach tanned goats, East India (Turwar bark tanned) good, and Australian (mimosa bark tanned) basils.

The following table shows the amounts of the various acids absorbed by the leather at the different temperatures when sumach tanned skiver was used:—

| Temperature. | 50°C. | 55°C. | 65°C. | 70°C. |
|---|---|---|---|---|
| Treatment. | Number of cc. N/10 acid absorbed by leather. | | | |
| Water ..... | ... | ... | ... | ... |
| Sulphuric acid N/50 ..... | 46.0 | 47.0 | 52.0 | ... |
| Hydrochloric acid N/50... | 42.3 | 42.3 | 46.3 | ... |
| Formic acid N/50..... | 41.5 | 25.6 | 32.2 | 41.1 |
| Oxalic acid N/50 ..... | 19.6 | 17.4 | 24.8 | ... |
| Sodium bisulphate N/50 .. | 47.6 | 52.4 | 56.2 | 48.3 |

It will be noted that the amounts of acid absorbed by the leather (skiver) in this case are much smaller in quantity than in the case with bark tanned calf. This is no doubt partly accounted for by the difference in thickness of the leather; the weight of leather in this particular case, though of the same superficial area as used in the previous experiments, was approximately one-seventh of the weight of the pieces of calf.

At 50 degrees C. and 55 degrees C. the pieces of leather were to all appearances similarly affected, being quite uninjured. At 65 degrees C. the pieces unaffected, so far as feel and general appearance goes, were the ones treated with water only, sulphuric acid and sodium bisulphate, and formic acid; those treated with oxalic, sulphuric, and hydrochloric acids were completely ruined.

Of the three pieces of leather immersed at 70 degrees C., the piece of leather treated with sodium bisulphate was rendered quite useless, but contrary to expectations those treated with plain water and with N/50 formic acid were quite sound good leather on removal and drying.

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EAST INDIA TANNED (TURWAR BARK) GOAT.

| Temperature. Treatment. | 60°C. | 65°C. | 70°C. |
|---|---|---|---|
| | Number of cc. N/10 acid absorbed by leather. | | |
| Water | ... | . . | ... |
| Sulphuric acid N/50 | 83.6 | 62.8 | 7.20 |
| Hydrochloric acid N/50 | 73.3 | 60.5 | ... |
| Formic acid | 53.6 | 47.8 | ... |
| Oxalic acid N/50 | 54.1 | 43.8 | ... |
| Sodium bisulphate N/50 | 78.0 | 78.6 | ... |

*Condition of Leather.*—At 60 degrees C. the whole of the pieces of leather appeared sound with the exception of the one immersed in hydrochloric acid, which had shrunk slightly and become somewhat dark in color.

At 65 degrees C. the piece treated with hydrochloric acid was much worse than when immersed at 60 degrees C., having become quite pelty, drying as hard as horn, and shrinking to about one-quarter its previous size. The leathers treated with oxalic and sulphuric acid, though damaged, were not nearly so detrimentally affected as those treated with hydrochloric acid.

The pieces treated with formic acid, bisulphate, and the one immersed in water, had apparently suffered no serious injury.

The piece treated at 70 degrees C. with plain water appeared to be quite uninjured.

SUMAC TANNED GOAT.

| Temperature. Treatment. | 60°C. | 65°C. |
|---|---|---|
| | Number of cc. N/10 acid absorbed by leather. | |
| Water | ..... | ..... |
| Sulphuric acid | N/50 84.0 | N/25 90.8 |
| Hydrochloric acid | N/50 79.0 (N/12.5) 78.2 | N/25 69.3 |
| Formic acid | N/50 14.3 | N/25 16.6 |
| Oxalic acid | N/50 15.0 | N/25 10.5 |
| Sodium bisulphate | N/50 77.3 | N/4 71.5 |

*Condition of Leather after Treatment.*—As in previous experiments at a temperature of 65 degrees C. with this strength of acid (N/50) the pieces treated with formic, bisulphate of soda, and water were quite sound leather, whereas those treated with hydrochloric, oxalic, and sulphuric acids were seriously damaged. Of the three latter the piece treated with sulphuric acid was the best and that with hydrochloric acid much the worst.

The experiment of immersing pieces of leather in acid solutions of double the strength employed in previous experiments was tried. It was found that all the pieces with the exception

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of those treated with formic acid were seriously affected, though treated at a lower temperature, namely 60 degrees C.

AUSTRALIAN (MIMOSA TANNED) BASILS.

Temperature:—60°C.

| Treatment. | Number of cc. N/10 acid absorbed by leather. |
|---|---|
| Water .... ..... | ... |
| Sulphuric acid ..... | 62.7 |
| Hydrochloric acid..... | 47.7 |
| Formic acid..... | 30.6 |
| Oxalic acid ..... | 33.9 |
| Sodium bisulphate ..... | 55.4 |

At this temperature (60 degrees C.), as in the case of the other leathers, the most seriously affected leather was the one treated with hydrochloric acid, those treated with oxalic and sulphuric acids were injured, whereas those treated with sulphuric acid and sodium bisulphate, formic acid, and water were apparently uninjured.

It will be seen that the above experiments show that the amounts of acid absorbed do not greatly vary upon the different leathers, and that in every case a greater proportion of sulphuric acid is taken up by the leather than is the case with any other acid. Hydrochloric acid is also absorbed by the leather in considerable amounts. The quantities of the two organic acids absorbed by the leather are very much smaller than with the inorganic acids. The temperature does not very seriously affect the amount of acid absorbed by the leather, but on the other hand it does materially affect the condition of the leather.

In view of the fact that it has often been stated that samples of leather on analysis were shown to contain an amount of acid equal to 6-10 per cent. on the weight of the leather, it was thought of interest to confirm this by ascertaining the exact amount of acid that was taken up by the leather in the dyeing process, and the influence of the concentration of the bath on the amount of acid absorbed.

It will be noted that the above experiments have been done on leathers of equal size and not of equal weight. Taking the average weights of various leathers, and calculating on the maximum amount of acid absorbed by the leather at various temperatures, it was found that the percentage amount of acid absorbed by the leathers was as follows:—

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MAXIMUM PERCENTAGE OF ACID (BY WEIGHT) ABSORBED.

| Acid. | Calf. Per cent. | E.I. Goat. Per cent. | Sumac Goat. Per cent. | Skiver. Per cent. | Basils. Per cent. |
|---|---|---|---|---|---|
| Hydrochloric.... | 2 | 2.9 | 4.0 | 8.0 | 1.8 |
| Sulphuric ..... | 3 | 4.5 | 6.0 | 11.6 | 3.2 |
| Formic..... | 0.9 | 1.5 | 1.7 | 6.3 | 1.5 |
| Oxalic ..... | 1.6 | 3.5 | 0.8 | 5.7 | 2.0 |

Looked at more from a practical than from a scientific standpoint, the most interesting points in connection with these experiments are:—

1. There is little liability of injury to leather if well tanned by immersion in water under 60 degrees C.

2. The amount of acid absorbed by the leather is practically the same no matter what the concentration, providing that sufficient excess is employed.

3. Any excess of acid not absorbed by the leather conduces to rapid disintegration of the leather at a much lower temperature than would otherwise be the case.

4. There is much less liability of damage to goods when using formic acid than any other of the acids mentioned.

It is proposed to continue these experiments in the direction of finding the exact amount of tendering of the fibre that has taken place under the varied conditions, and to perhaps extend the research in other directions.—Leather Trades Review.

## REVIEWS

**The Deterioration of Coal.** S. W. PARR AND W. F. WHEELER. *J. A. C. S.*, 1908, 6, 1027-1033.—Cooperative experiments conducted by the State Geological Survey and the Engineering Experiment Station of the Univ. of Ill. have developed some very valuable facts in regard to the deterioration of coal under different conditions.

Twenty-nine samples were taken at the face of the vein, quartered and sealed in galvanized cans, shipped directly to the laboratory, and transferred at once to "Lightning" or Putnam jars. Twenty-one other samples were sealed in Mason jars, and all were set aside for a period of 10 months. When opened at the expiration of this time, 26 of the samples in the Putnam jars showed a slight gas pressure which ignited with a strong blue flame, burning from ½ to 6 inches above the top of the jar, re-igniting two or three times upon covering and re-testing. Owing to their imperfect seal, none of the samples in Mason jars gave the above test. The phenomenon noted in the above tests on the Putnam jar samples cannot be ascribed to any weathering process, but to

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the fact of the removal of the coal from its natural conditions of pressure, etc. In another series of tests air-dried samples were sealed in Putnam jars, the same being about ¼ full instead of entirely so, as in first instance. At the end of 18 months all showed a positive absorption of oxygen. Less than 1.5 per cent. oxygen and 2.0 per cent. carbon dioxide were shown upon analysis. Attention is also called to the loss in fuel value of freshly mined coal after shipment. Six cars were sampled at mine and again at destination, 4 to 7 days later. The average loss in B. T. U. was 122. Other comparative tests conducted at the St. Louis Coal Testing Plant of the U. S. G. S. and the Ill. Univ. show the fuel value loss due to ageing of samples. The average loss between the fresh samples and the same after 10 months was 365 B. T. U. or 2.5 per cent. All tests were conducted under as nearly similar conditions as possible, and the same type of calorimeter was used. For comparison with the above samples of 10 months standing, other new samples were collected, and analyzed within two weeks. The new samples had an average higher value of 356 B. T. U. or 2.4 per cent. A third comparison on new samples tested by the U. S. G. S. within 2 weeks, and by the Ill. Univ. soon after collection gave both plus and minus results with an average difference of only 29 B. T. U. or 0.2 per cent, which might be ascribed to other causes rather than the age of the samples. It seems evident, however, that the drop in values occurs within the first two or three weeks after the coal is taken from the vein, but the extent and rapidity of the change is difficult to determine. The theory is given that the loss is due to the exudation of gases from the coal upon being released from the pressure of the vein.

To show the loss due to oxidation or weathering, tests were made on pillars from 22 to 27 years old, and on the coal fresh from the mine. The pillar coal showed a loss of 423 B. T. U. or 2.5 per cent. Coal submerged in the mine for one year, and then exposed in pile one year showed a drop of 347 B. T. U. The exterior and interior of the pile being nearly identical.

A series of tests conducted by Mr. N. B. Hamilton show that submerged coal does not suffer loss through oxidation. On the other hand, exposures to ordinary atmosphere, to a dry atmosphere 85°-120° F., and with frequent drenchings, to atmosphere at 85° to 120° F., lead to a loss in the calorific value of the coal. These losses are largely over-estimated and probably do not exceed over 3 or 4 per cent.

**The Rational Treatment of Low Grade Stock for Upper Leather.** W. EITNER. *Gerber*, 1908, pp. 61-2, 89-90, 103-4, 117-118.—The exigencies of modern tanning require the disposal of a large amount of raw material unsuited for the production of chrome-tanned leathers for which stock of perfect grain is needed. Fortunately it is possible to tan material with defective grain so that it may be vigorously buffed and made available. The following deals with the working up of marketable products from such material, particularly kips.

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Even with high-grade kip stock, the proper softening from the dried state is not easy and becomes a matter of the highest importance in the case of inferior goods, having more influence on the product. At the present time kip stock softens much easier than formerly which is due to a small amount of salt added as a preservative before the drying. This however, does not help in the case of shrivelled skins or those of diseased cattle and energetic means are necessary to gain the desired softness required for the tanning process. This is furnished by the "strengthened" soak.

Some assume that a hide which has been damaged by putrefaction cannot withstand the action of alkali in the strengthened soak and that softening in water is preferable. It is true that hide substance which has rotted is irrevocably lost for tanning, for it is disintegrated by alkalies or even water; what is left however of sound tissue remains intact in the strengthened bath. At the same time the ferments and their products, some of which have solvent action upon hide fibre are destroyed. Soaking in water does not do this, but on the contrary, revives the fermentation process and the original damage is extended. The alkaline soaking has a greater power for swelling the hide substance, allowing large amounts of water to penetrate which is precisely the object of soaking. The writer was recently called upon for opinion in a case where especially inferior stock had been given for tannage and yielded a brittle leather of minimum value. The strengthened soaking and liming were recommended and there was no further trouble.

As to the working process, the weighed hides are first placed in a strengthened soak which has already been used, and left their 2 days with daily turning. The liquor is then drawn off, replaced by fresh water, and to this sodium sulphide equal to 10 per cent. of the weight of dried hides is added, either direct with stirring or else previously dissolved in hot water. Hides which are not dried, after one day's standing are completely saturated, but hard brittle stock requires an additional day or two. It must be emphasized that kips in the strengthened soak do not become soft in the same way as when pure water is used; on the contrary, because of the considerable swelling, they become firm and elastic to the touch. If it is demanded that they should be actually soft, it is merely necessary to place them in pure water. This is not at all necessary, since the real object of soaking, the impregnating of the tissue with water, is accomplished in the strengthened bath.

Although in the operation some hides are softened before others they suffer no injury if allowed to remain until the process is complete for all. This is not the case in the ordinary soak when the hides first softened must be removed to prevent injury through putrefaction and it is impracticable to hit the right moment for removal of each separate hide. Stretching of the hides is unnecessary during or after the strengthened soaking.

After draining from the soak, the hides are next brought into the lime pits. Here it is of advantage in many cases to sort the stock and

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reject those hides which have been injured by rotting as revealed in the soaking. It is not profitable to work these for upper leather and they are tanned for innersoles. They are brought into a straight lime pit in which after 4-5 days they are ready for dehairing.

That portion of the hides sorted out for upper leather is placed in a strengthened lime which has already been used; the hides remain here 4 days and are then transferred to a strengthened lime which has not been used; this is prepared from a previously used straight lime. For the strengthening 5 kilos of calcin are added for every 100 kilos of raw dry hides. Here the hides remain 4 days, or for very hard stock, 6-8 days. The strengthened lime is used because after soaking with sodium sulphide, the hides would swell too much in the pure lime and would not later acquire the mildness necessary for upper leather. For the same reason sodium sulphide is replaced by the milder calcin; in the pure lime pit or lime strengthened with sodium sulphide, the hides become stiff and elastic which is desirable for innersoles but not for upper leather.

A thorough loosening of the tissues ensues in the strengthened lime and the plumping may next be promoted by transferring to a fresh lime pit charged with water and 5 kilos quicklime to 100 kilos of dry stock; here the hides remain 4 days after which they are dehaired. After use, the liquor in this pit together with calcin is used for the fresh strengthened lime with the next batch of hides, and after use there is likewise transferred to the old pit and after use discarded. Three liquors are therefore required for each lot of hides each of which makes its round and is replaced. The regular renewal of the pits is very essential for inferior kip stock, and preferable in any case. The dehairing, after liming in this way is very easily effected; this is of significance in the case of stock with damaged grain which would be further injured by active mechanical treatment.

The succeeding operations are carried out in the usual way excepting that the treatment with water is limited because a special process is used for deliming, namely the salt bate which follows the stretching. This contains 6.6 kilos salt, 1.3 kilos conc. white hydrochloric acid 24°B. for each 100 kilos of butts, which remain 6 hours in this bath with frequent agitation. Here they are not only freed from lime but also become mild and smooth in grain. For stock with grain injured by rotting which must in any case be buffed, it is sufficient to wash with lukewarm water after the bate. For better grained stock, the hides are placed in a light bate of hen or pigeon dung made up warm at 30° C. in which they are reeled 2 hours, followed by 1/2 hour reeling in lukewarm water which completes the preparation for tanning.

Cowskins are treated in the same way as kip but the amount of sodium sulphide is reduced in the soaking, with fresh or moist hides to 3 per cent.; with older and harder stock, to 5 per cent. The liming is as with kips, although the calcin may be reduced.

The tanning process is a combination of two stages, the first tanning with alum, and the complete tanning with vegetable tanning material.

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The first tanning is combined with a pickling in which the following liquor is used. Ten kilos of salt are dissolved in 2 hectoliters of water, 1 kilo of sulphuric acid added and finally a solution of 6 kilos of alum which may be economically replaced by 4 kilos of 15 per cent. aluminum sulphate. Four hours suffice for the first tanning in drums or the butts are placed in vats, covered with the liquor and left 2 days with frequent turning. The presence of the pickle makes the tanning different from an ordinary alum tanning; the tanning is more even, but much less in extent, which is of importance in its influence upon the vegetable tannage. In chrome tanning at times an alum pre-tanning is combined with a pickling but this hardly seems necessary since both stages are of the same character. It is quite different however in a combination process with both mineral and vegetable materials.

The vegetable tanning which follows is carried out either partly in drums or else entirely in vats which last is preferable producing a plumper leather with greater surface.

As a rule, Japonica is used, which gives a light tannage. The writer has found that sulphited extracts designated as "cold soluble," especially Mimosa D are well suited. If the principal part of the tannage is to be effected in the vat, four liquors are used for the first stage. The last liquor is of 10° barkometer strength made up from water and old vat liquor; after being used once it becomes the third liquor, then the second, and finally the first. To this first liquor, before introducing the hides from the alum and pickling bath, are added 2 kilos antichlor per 100 kilos butts in order to fix the pickling acid and prevent formation of a brittle leather. The hides remain 2 days in each liquor. After the 8 days preliminary tanning, the leather is completely tanned in the wheel with a liquor of 25° prepared from fresh Mimosa D extract which is strengthened every 2 hours since it rapidly weakens. With heavy leathers the strengthening goes to 28° at the highest. The leather is tanned through in 12-16 hours.

If the tanning is carried out in vats, 8-10 liquors are necessary, the last being made from fresh Mimosa D extract at 25°. As a rule the liquors must be strengthened, say from the fifth downward.

The leather from the tannage in drums is always more densely tanned than that treated in vats. This is not desirable for all applications of the leather; if demanded it can be attained by an additional tannage which permits a sorting of the products of the main tanning operation.

After tanning the leather is sorted for splitting or shaving. The grain splits obtained or the pared hides are next milled in the drum until they become soft and are greased with 5 per cent. of a mixture of 70 parts of fish oil and 30 parts of vaseline oil. The leather is milled 1½ to 2 hours with this mixture, then dried and stacked at least 8 days.

Leather sorted out to be sold by weight and also sides with damaged grain are subjected to an additional tannage. The leather is milled until quite soft and then tanned with strong liquor. The usual pre-

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liminary treatment with weak liquor is unnecessary since the leather has already been uniformly tanned and the light greasing prevents a too sudden action of the strong liquor. Japonica is used, 40° in drum tanning, and up to 35° for tanning in vats, which slower process gives better results. R-Catechu, an extract prepared from Mangrove bark is better suited for a filling material which is the requisite here. The dark red color which it gives the leather is not objectionable for some purposes.

If the leather is required dry to the touch it is next liquored using a soap liquor. The writer's receipt is: for 100 kilos of leather, 3 kilos of liquor soap, 3 kilos moellon and 2 kilos mineral oil stirred together and gradually diluted with 25 liters of warm water. In this the leather is milled one hour, then hung up to dry, and finally stacked for 3 days. If the flesh side is to be dyed, which is generally the case, the leather is softened in water, milled and then dyed using auramine (for yellow), aniline blue, etc. The dried leather for plain currying is now buffed on the grain and for this the pieces with damaged grain are selected. As a result of the prescribed treatment the leather has acquired at least a soft grain which permits sufficient buffing to establish a genuine grain. The buffed leather is blackened dry with thick black while non-buffed leather still wet is blackened on the table.

If the leather is to be greased, liquored or unliquored leather may be employed; the latter after shaving and washing is dyed on the flesh side, stretched, dried, buffed and blacked. Both sorts are smeared on the flesh side with a mixture of 2 parts of moellon, 1 part vaseline oil and 1 part tallow; the leather is finally rolled and then stretched in frames.

The flesh splits obtained from the grain splits are tanned in ordinary extracts, either oak-wood, or quebracho, or mixtures of both and then further curried for brown or black dressing. R-Catechu is especially suited for this tanning, giving considerable increase of weight; the color is not improved to be sure, but this is of little consequence with black waxed leather.

Dyed leather may also be made by the combination tanning process described; this requires a sound perfect grain in the raw stock. The grain splits are first milled in water then after tanned with sumac 3 hours in the drum, at 50° C., 6-8 kilos sumac for 100 kilos of leather. After rinsing, the leather is mordanted with ½ kilo tartar emetic to 100 kilos leather in 50 liters water. If the dyeing is to be on both sides, it is carried out in the wheel; for merely dyeing the grain, the dye is applied on the table. Aniline colors are used and added in solutions little by little to the bath until the desired tone is obtained. The dyed leather is rinsed in water, racked and oiled on the grain, best with mineral oil; the linseed oil formerly used dries and makes the leather brittle; the neat's foot oil now frequently employed easily oozes out.

If the leather is to be dyed on the table, the very dilute color is applied with a soft brush, followed by stronger solutions. Currying for satin leather is very popular; the leather sorted for this should not be

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too much damaged in grain; after splitting it is tanned with sumac in the same way as the leather for dyeing and then liquored. Greasing with liquor is chosen because the leather although it becomes very soft, acquires a dry feel which is demanded in satin leather. The leather is next dried and piled 14 days, during which the fat becomes fixed. It is then milled, racked and again dried, and is ready for buffing. With satin leather, this operation removes the outer surface of the grain, leaving it firm and more flexible, and much improved in appearance. Hand buffing is preferable to machine work. In the following blackening, the usual black thickened with starch or glue is not used. The special black used is prepared by dissolving 3 pints pure log-wood extract in 100 pints hot water and boiling with 0.3 pint red chromate of potash; then to 100 pints of such solution 6 pints of Marseille (or liquor) soap are added and left to dissolve. After cooling, 250 pints of Neuberblack are added, little by little causing the black to thicken by precipitation or "break." With good stirring the precipitate remains finely divided; with insufficient stirring, too rapid addition of the black or too hot an extract solution, lumps are formed which cause smearing.

After blacking, the grain is oiled with mineral oil, dried, stretched in frames, then rolled in the satining machine with the hot roll after first applying the satin lustre. There are many complicated receipts for this; the simplest is made by melting 2 pints stearine in 100 pints boiling water, allowing to cool as long as the stearine will remain fluid, then adding ½ pint ammonia and continually stirring until the resulting paste has cooled to about 35° C. This is spread with a brush over the grain and allowed to dry. The grain is next brushed with a stiff brush and satined with the hot roller.

Although in the description of the foregoing tanning process and the preparation of the butts, inferior raw stock was in mind, the processes are suited for better material.

**Hide Powder Methods.** R. D. WESTENFELDER. From *Hide and Leather.*—Simply washing hide powder with water does not make it of uniform absorptive power. The idea of chroming hide powder, first proposed by Berthold Weiss, and later more fully developed by the A. O. A. C., and the A. L. C. A., at times gave uniform results, and at other times did not. The cause for this lack of agreement arises from the fact that the powder is washed with tap water of varying degrees of temporary hardness, and only within the past year has this fact been made known. Distilled water,—"a neutral body"—should always be used, since it has been shown that alkaline hide powders do not absorb all of the tannin, and ground sole leather is almost stripped of tannin by treatment with as little as 15 drops of 10 per cent. ammonia water per gallon of water. The author sets forth "an ideal method," which has been used by him since about 1896. Neither the condition of the rawhide nor the parts of same, "shank, belly or butt," seem to influence the uniformity of results when treated by his method. Briefly

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stated, the method is as follows: Into a three gallon crock, put 300 grams of hide powder and add water until crock is one half full. Now add 20 grams of bisulphite of soda and 25 cc. of 66° sulphuric acid, and stir thoroughly. Wash, by decantation, until nearly acid free, and add solution of sulphate of aluminum, stir thoroughly and neutralize with dilute ammonia water until slightly alkaline. Wash free from sulphates and soluble hide, by siphoning through inverted funnel with cotton plug in the stem. During the washing, the powder should be frequently stirred with fresh portions of distilled water and allowed to settle. After washing, the powder is squeezed out by hand, finely broken up, and after one hour, covered with water containing 10 drops of glacial acetic acid per liter. Here it will keep for 7 or 8 days. Before use for analysis the required amount is put into funnel with cotton plug in stem, and washed with successive 200-300 cc. portions of distilled water until free from sulphates and soluble hide.

Since it is the acid radical in chromed powders which gives the uniform absorptive power, this power decreases with age and basicity of same; hence the failure of dry chromed powders and those squeezed below a certain moisture content. The author's method claims, at all times, to give a uniform powder, even from inferior quality of hide. Sulphate of alumina is added simply to make the powder squeeze drier, and in no way influences the absorptive power. By using powder prepared as above, no caramelization of non-tannin residues takes place as the acid is neutralized with ammonia.

To obtain ground hide powder, only the shanks of the hides are used. These are cut off in the beam house, flesh cleaned, and hung up until bone dry. They are then soaked in cold water, 10 to 12 hours, cut into pieces one to two inches square, dried, chopped fine with a Brecht cleaver chopper, and finally ground in an ordinary grain or bone mill. Both strictly granular, and extremely powdery hide powders should be avoided, the best results being obtained from those which are semi-granular. Our meagre knowledge of tannins and non-tannins, does not permit the statement, that one is a tanning agent and the other not. "Flasiewetz has suggested that tannins should be regarded as gummides or dextrides, and the formation of reducing sugars—by the action of acids—is due to this action on the gums." Fairly strong non-tannin solution when poured into strong alcohol, gives bodies resembling dextrine. Due to action of excessive acidity, some tannery liquors become ropy and even jelly, which extremely colloidal nature of the non-tannins, stops the tanning process, except by those tannins of a more distinctly sub-crystalline nature. The same non-tanning effect has been observed, when the colorless non-tannin filtrate, from a weak tan solution is faintly acidified with sulphuric acid and repeatedly returned through the hide powder in the funnel. The final filtrate is no longer colorless, the acid having removed matter only feebly held by the hide.

The author believes, that under normal conditions, some of the so-called non-tannins, enter into combination with hide matter to form

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true leather substance. To what extent this takes place in practice, is not definitely known, and exception is taken to Mr. R. A. Earp's attempt to prove the extent of such combination, (see Jour. A. L. C. A., Vol., II., No. 4). Mr. Earp's deductions were based on drum liquors before and after hides went in, without making any correction for dilution by the weak liquors in the hides entering drum. The author prepared a quantity of non-tannins from chestnut liquor, made with distilled water. This was done by completely detannizing said liquors by repeated treatments with hide powder, concentrating filtrate in vacuo, and finally drying on water bath. The resulting mass was then powdered, dissolved, and analyzed for non-tannins, "when it was found that 50 per cent. of the total matter had been absorbed by the hide." The conclusion is, that the non-tannins before concentration, contained tanning substances not indicated by the gelatine test. The redissolving of chromium hydrate, precipitated by ammonia, in the presence of sugar, and some organic acids, is given as a parallel phenomenon. Non-tannins strongly influence the tanno-gelatine precipitate, as shown by Dr. Stiasny, in "Der Gerber," see Jour. A. L. C. A., Vol. II, No. 7, Vol. III, No. 1. A tannin solution so weak as to give only a turbidity with gelatine, gives a flocculent precipitate upon the addition of oak-wood non-tannins. Also a fresh tan solution with basic chrome salts, gives at first only turbidity, a precipitate not forming for several days. Gallic acid has a similar action to that observed by Dr. Stiasny with oak-wood non-tannins. Instances are given where the "filter bell method" gives highly colored clear percolates, containing both soluble hide and tannin. Some tanning materials, upon continued extraction with boiling water, show persistent test with gelatine, but upon concentration of the liquid, these tannin-like bodies precipitate, become insoluble, and inactive to gelatine. These insolubles may be considered either as anhydrides of the tannins, or of "some of the constituents of the so-called non-tannins," In the latter case, "it might be considered in the light of gallo-tannic acid, as being the first anhydride of gallic acid." Or, the non-tannins may be likened to purified and dialyzed caramel which has both "soluble and insoluble modification." "The latter has its solubility restored by the action of alkalies, followed by that of acetic acid and subsequent dialysis"—Watt's Dict. Chem.

In light of these statements, hide may be considered as having the power to cause this insoluble modification, with the results that, the non-tannins become fixed in its fibers to form pure leather substance. Considering the insolubles as strictly non-tannin in nature, the statement that all are anhydrides of tannins does not hold good. If this is the case, the shaking of unfiltered tan solutions with hide powder might cause an error in the non-tannin figure, since the insolubles would be more soluble in the detannized solution. "The fixation of the non-tannins by the hide, most probably accounts for the differences in the degree of tannage, as obtained with various tanning substances." The part which the non-tannins play in the formation of leather is also indicated in the

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analysis of the leather itself, when it developes that the ratio of tannins to non-tanning in partially tanned leather, is as well contained as in that which is fully tanned. The degree to which this combination takes place is not determinable in the laboratory, and in practice, is influenced by liquor conditions, methods of handling, etc., or even by the nature of the non-tannins.

Because of the extremely slow diffusion of colloids, the shaking or stirring, in non-tannin determinations, must be thoroughly done, otherwise, the dilution factor for the water in the wet hide does not give correct results, since equilibrium has not been established. The shaking or stirring should not stop the moment the solution ceases to react with gelatine, but should continue until the dilution is complete. This condition is not brought about by the milk shaker because the agitation is not vigorous enough to cause perfect diffusion, and the non-tannins are practically held out. The time of agitation should not be limited, as some foamy liquids, especially hemlock, require more time for complete detannization. To replace the milk shaker, a centrifugal stirrer was devised, and has been used for years with excellent results. A cut of same is here appended, and no explanation is necessary. The brass cone has from 4000 to 5000 R. P. M., thus strongly projecting the hide particles against the walls of the glass, forces the liquor into them, and proper diffusion ensues. Less speed increases the non-tannin figures. The method of operation is as follows:

To 20 grams of squeezed hide powder, in stirring bottle, add 200 cc. of tan solution, five drops of glacial acetic acid, and stir five minutes or until foam disappears. Now add 20 grams more hide powder and proceed to stir as above. Pour the whole magma into funnel with cotton plug in stem, let drain, gently pack hide powder in funnel, and return percolate until clear. In obstinate cases, liquor is squeezed from the hide, and filtered through asbestos in carbon filter.

Acetic acid is added to the tan solution to promote more complete absorption of the tanning substances. This method is preferable to that of trying to regulate the acidity of chrome powders, since the amount added is the same in every case, and results in uniformity. Non-tannin residues are not visibly changed by its use, and its presence is especially necessary for complete detannization of bisulphited extracts and alkaline tannates. Furthermore, it accords with tannery practice. Acetic acid lessens the absorption of gallic acid, while salts have the opposite effect.

The author supports the view that the affinity of hide for tanning rather than for non-tanning substances, is selective and physical, depending on the equilibrium established. Reference is made to articles by Gardner and Carter, who have shown that cotton fiber saturated in a 0.5 per cent. tannic acid solution will still absorb in a solution of 0.2 per cent., the balance being reached at 0.02 per cent. where some tannic acid goes back into solution. The absorption is greatly increased in the presence of acetic acid. The assumption is made, therefore, that in the

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FIG 1

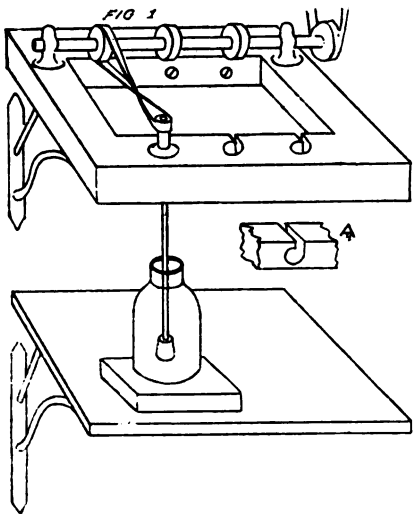
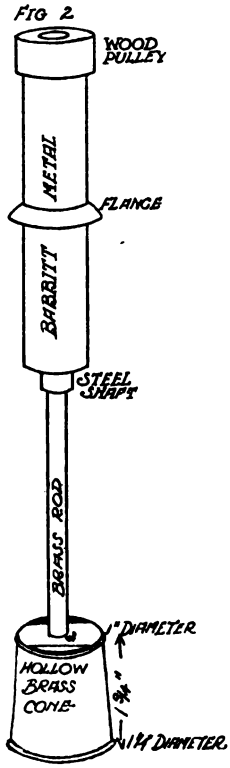



FIG 2

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presence of non-tannins, the tanning substances are not all absorbed by one shaking, but only by repeated percolations through hide powder. This is especially true of the very weak tan solutions where the point of balance is nearly reached. The A. L. C. A. method of squeezing the non-tannin liquor from the hide is in error since those tannins which are not firmly fixed in the hide are squeezed out, and react with gelatine in the non-tannin filtrate.

The author finds the gelatine test to be "illusive," giving both positive and negative results. Some non-tannin solutions which previously gave no reaction, will after heating and standing, give a reaction with gelatine. This may be due to the solvent power of the non-tannins, or of an excess of gelatine, or of both on the tanno-gelatine. With his method, tannins are never found in the non-tan filtrate, and are rarely ever tested for, but with hide powder four or five days old, tests are always made for soluble hide. This test is made with Merck's gallo-tannic acid, and in case of reaction, the filtrate is treated with from five to ten milligrams of the above, and percolated through the hide powder until clear. Ninety per cent. of the gallo-tannic acid is absorbed by the hide, the other ten per cent. being a negligible quantity.

Tan solutions should be filtered before stirring with the hide powder, since in the detannized liquor, the so-called reds are more soluble than in the original liquor, and leads to an error in the non-tannin figure. The more uniform non-tannin figures by the filter-bell method, on materials of the same kind and manufacture, may result from the fact that the insolubles are subjected only to the original liquor.

The author uses stronger solutions for analysis than called for by the official methods of the A. L. C. A., and would use still stronger ones were it not for the difficulty in observing the clarity of the soluble solids filtrates. The following quantities per liter are used: Liquid oak, chestnut and hemlock extracts, 21.5 to 22.0 grams, dry quebracho and mangroves, 8 to 9 grams; liquid quebracho, 16 to 18 grams, and other extracts in proportion to give from 0.42 to 0.46 gram of total solids, residue per 50 cc. of solution. Amount of hide powder, 40 grams wet, equivalent to 12 grams dry. Materials for extraction, except spent barks, etc., are taken in such quantities as to yield a solution of the same total solids as given above for extracts. One hundred parts of water are taken for 1 part of material, and the percolates, which are always collected outside the extraction, are concentrated in vacuo to one half or one liter as required. Extractions from spent materials are necessarily weaker, and require from 20 to 30 grams of wet hide powder (6 to 9 grams dry) for 200 cc. of solution. For these weak solutions the Lowenthal method may be used with equal accuracy where the results are merely for factory control.

In support of his belief that the absorption of non-tanning substances increases in the presence of tannin, the author cites some experiments of Dreaper and Wilson (J. S. C. I., 1906, p. 515, et seq.), which show that the absorption of gallic acid constantly increases as the tannin con-

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tent of the solution is raised. What is true of gallic acid is also claimed to be true for complex non-tannins, and the opinion is expressed that the absorption of gallic acid by the hide is permanent. The presence of acetic and hydrochloric acids greatly reduce the absorption of gallic acid.

**Book-binding Leather From Nigeria.** M. NIERENSTEIN. *Quart J. Inst. Comm. Research in Tropics, Liverpool Univ.*, 1908, 3, 44-46.—The skin under examination was a goat-skin, evidently incompletely tanned. Analysis: Water, 5.72; fat, 10.06; extractives, 6.54; ash (Al, Na, Mn, Ca, $PO_4'''$, and $SO_4''$, 42.83 per cent. being alumina), 5.91; and insoluble, 71.77 per cent. Nitrogen 14.26, as against 17.47 per cent. in goat skin. Tannin mostly pyrogallol with some catechol. The author states that catechol tannins should not be used in book-binding leathers, "red decay" or "rot" resulting therefrom.

## PATENTS

**Process for Decolorizing Tanning Extracts, French Patent No. 383,890.** C. FEUERLEIN. Salts of chromium are used for the decolorizing treatment.

**Process of, and Extracts for, Tanning, French Patent No. 384,080.** J. P. RASMUSSEN. In 100 parts of boiling water, dissolve, 4 parts by weight of cashew, 10 of aloes, and 25 of sodium hydroxide. Add 75 parts of alum and dilute with hot water. To the water in the vat containing the hides, add sufficient of the above mixture to raise density to 15° B. The hides next pass to a weak sulphuric acid bath, and then receive the ordinary treatment with tannins. Time of actual tanning about 70 days.

**Decolorization of Extracts Containing Tannin, U. S. Patent No. 889,059,** to A. J. STIEGELMANN and E. DEHNEL, Ludwigshafen, Germany. The process of decolorizing extracts containing tannin consisting in heating the said extracts in aqueous solution with a formaldehyde sulfoxylate.

**Machine for Dressing Hides, Skins, Etc., U. S. Patent No. 889,146,** to J. W. O'DONNELL, Leicester, England. An improved leather-working machine on the order of a serial table machine.

**Liquid Agitator, U. S. Patent No. 890,315,** to J. and M. VALIQUETTE, Cumming's Bridge, Ontario. An agitator for tanning processes, comprising a vat in which the hides are suspended by hooks attached to bars on each side of the vat. An endless chain, having paddles attached, runs down one end, along the bottom, up the other end of the vat, and over sprockets above the vat. Means for supporting and actuating this chain are supplied and when running, the movement of the paddles serves to agitate the liquor. Partitions prevent the hides from coming in contact with the chain.

**Manufacture of Artificial Leather, English Patent No. 6,216,** L. V. GUILLETEAU, Paris. 0.5 kilo of balata gum dissolved in toluene, and 1.8 kilos of dextrine are intimately mixed with 72 litres of water at 95°C. A mixture of 4.5 kilos of glycerine, 0.07 kilos sodium silicate and 18.13 kilos of gelatine is then added, and after solution the

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whole mixture is kneaded with 3 kilos of ramie fibre in a steam-heated kneading machine. The mass is then dried at 80°C, and passed through a succession of presses at 100°C, the pressure being gradually increased. The plates are then immersed in formaldehyde for 20 minutes and dried. A larger proportion of balata gum gives a stronger product. For the manufacture of pneumatic tire covers the following is used: Water, 47.5; dextrine, 1.8; glycerine, 4.5; sodium silicate, 0.07; gelatine, 18.13; balata gum and toluene, 25; and ramie fibre, 3 kilos.

**Manufacture From Split Leather of a Waterproof, Fast Colored Leather Which is of Equal Value With Upper Grain Leather, English Patent No. 28,743,** to S. PIANKO AND M. KNASTER, Wloclawek, Russia. The desired coloring matter is mixed with castor oil to a butter-like consistency, after which a solution of celluloid is gradually added with constant stirring. The mixture consists of 9 parts of celluloid to 1 to 2 parts of castor oil. If necessary, the mass is diluted with amyl acetate or acetone. After rubbing in the mixture, the split leather is finished in a graining machine, and finally dried at about 40°C.

**Manufacture of Many Colored Leather Varnish, English Patent No. 21,906,** to W. and G. FIELDMAN, Berlin.

**Process of Making Artificial Leather, French Patent No. 380,302,** to F. BAUM. The muscles, etc., are chemically treated and pulverized. The resulting mass is then tanned, dried and spun into threads resembling silk.

**Process for Purifying Gelatine, German Patent No. 185,862,** to M. SIEGFRIED. Aqueous gelatine solutions are treated with ammonia, alkali hydrates, soluble organic bases, or ammonium or alkali salts of feeble acids.

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## FILTRATION.[1]

*By F. H. Small.*

The Committee whose report is contained herein was appointed to study the question of the filtration of tannin analysis solutions, especially the method proposed by Reed at the last annual meeting and published in the Journal, Vol. II, No. 11, pps. 420-426. Several of the members originally appointed on the Committee were unable to serve and those actually taking part in the final work were Messrs. Oberfell, Van Gyn, Reed and the Chairman, Mr. Loveland assisted in the preliminary work and Mr. Westenfelder sent in some suggestions.

In response to the Chairman's preliminary letter calling for suggestions as to the conduct of the work, no definite propositions were presented save one by Mr. Westenfelder relative to a method of filtration used by him for several years and which will be found later in the report. The Chairman therefore sent out the following directions for preliminary work:

Determine by the following methods the soluble solids value of as wide a range of analysis solutions as are available including at least one perfectly clear solution. In every case collect as many successive 100 cc. portions through each filter as the time at your disposal permits. It is desirable that for each comparison enough of the solutions be made up so that the identical solution can be used for all the work. The following data are desired:

Total solids, weight and per cent.

Soluble solids, weight and per cent.

Time to collect each successive 100 cc. in order.

Character of filtrate as to clearness.

Condition of filter at close of filtration.

I. Official Method.

II. Official Method except that two 75 cc. portions, each used for one-half hour, are to be employed for the preliminary saturation of the paper.

III. Same as II except that S & S No. 602 hard filter paper is to be used.

IV. The Reed asbestos-kaolin method, JOURNAL A. L. C. A., II., pp. 420. It will be well to try different amounts of kaolin and asbestos.

[1] Report of the 1908 Committee.

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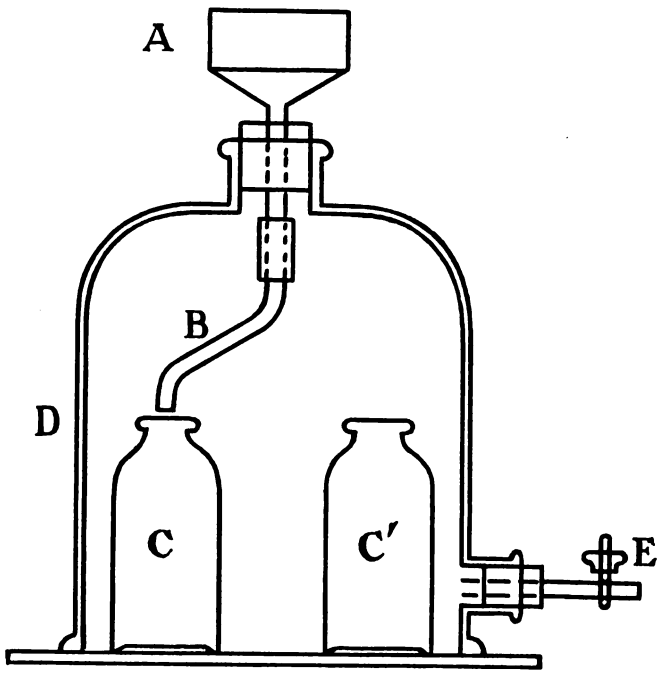
The Chairman has found a modification of the Reed apparatus as pictured herewith simpler and easier of manipulation for experimental purposes. A is a porcelain perforated funnel passing through a rubber stopper inserted in the mouth of the bell jar D. B is a glass tube connected to the end of the porcelain funnel. E is a cock which is closed after the bell jar




has been exhausted. C,C′ are 4 oz. wide-mouth bottles. By rotating A, B may be made to deliver into the different bottles successively. The apparatus used by the Chairman will hold five bottles.

It was hoped that by method II a sufficiently complete saturation of the filter paper might be attained to permit the use of S. & S. No. 602 hard filter paper, a result which to the Chairman seemed desirable because of the readiness and certainty with which a perfectly clear filtrate is obtained by this paper,—a result not always secured with official No. 590 paper. Two 75 cc. portions, each used for one-half hour to saturate the filter paper

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proved to have no practical advantage over one 75 cc. portion used for one hour and by this method the No. 602 hard filter paper still showed so great absorption as to render its use inadvisable.

Specimen results were as follows:

| Kind | Total Solids Method I | Soluble Solids II | III |
|---|---|---|---|
| Hemlock | .6724 | .5757 | .5768 | .5646 |
| Quebracho | .5462 | .4943 | .4943 | .4799 |
| Chestnut | .5864 | .5842 | .5846 | .5823 |
| Liquor | .6671 | .6561 | .6529 | .6509 |

The results by the Reed method at the hands of most of the Committee were not satisfactory. Mr. Loveland called attention to the difficulty of using the method in a laboratory not supplied with steady and fairly strong water pressure, as also to the possibility of difficulty in securing a satisfactory asbestos. Mr Oberfell rightly criticised the apparatus suggested by the Chairman, on the ground that the successive 100 cc. portions were left in the rarified atmosphere of the bell jar and so an error introduced by evaporation. The Chairman realized that the apparatus was open to this criticism when he suggested it, but it had proven so convenient for the sort of work to be done that he regarded its advantages as more than offsetting its disadvantages.

The Chairman had meanwhile been carrying on experiments by the Reed method with a rather wide range of materials, using varying amounts of asbestos and kaolin, different degrees of exhaustion, etc.

For the final work of the Committee he sent out four samples of extract and three of liquor together with the following directions which embodied the results of his experience.

I. Follow exactly the official procedure for the determination of total solids and soluble solids in extract analysis.

II. Follow the Reed method as outlined below, the analysis solutions being cooled to 20° as in the official method.

Use the apparatus pictured herewith and proceed as follows: Close cock B, and exhaust the 500 cc. flask to an approximate 16" vacuum through the side tube C which is conveniently fitted with a short rubber tube and pinch cock so that it may be fastened to a T-tube, one arm of which is connected with the air exhaust and the other with the mercury gauge. When exhausted to the requisite degree close cock C. Connect the side tube of the 250 cc. flask to the air exhaust, which also is conveniently con-

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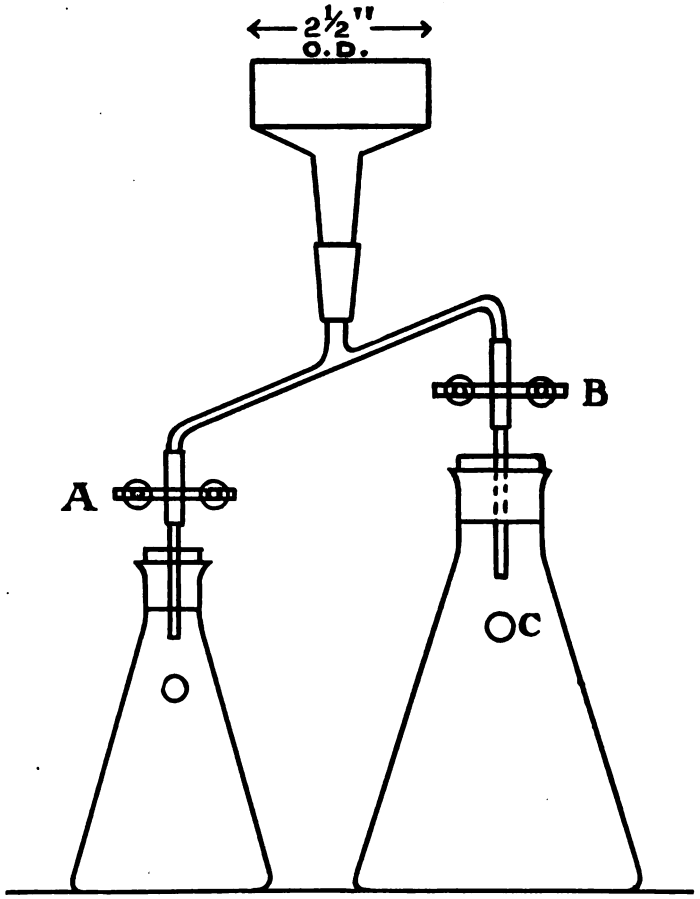
nected to a mercury gauge by a T-tube. Start the air exhaust, cock A being open, and throw on the filter plate 50 cc. of the solution to be filtered, to which has been added 1½ grms. of asbestos. Allow the air suction to pull this down to a firm mat. The success or failure of the filtration depends mainly on this




stage of the process, it being essential that a uniform, firm, well-interlaced mat be obtained and it saves time to stop and begin again if a satisfactory mat is not obtained. A little practice enables one to secure a satisfactory mat with small likelihood of failure. The air suction still being on, throw on the filter 50 cc. of solution containing 1½ grms. of kaolin; run the vacuum up to about 16" adding fresh solution as is needed to keep the asbestos

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well covered until 150 cc. in all is run through into the 250 cc. flask. The filtrate should now be perfectly clear, but if not more must be run through into the 250 cc. flask. Cock A is now to be closed and B opened and the necessary 100 cc. of filtrate collected in the 500 cc. flask. On account of the dimensions of the 500 cc. flask the 100 cc. is best measured by the amount thrown on the filter. If it is desired to watch the degree of exhaustion of the 500 cc. flask the flask may be connected up with a mercury gauge by means of the side tube connection. The asbestos used must be of a woolly nature and must have been digested over night in a fairly strong hydrochloric acid, then washed free of hydrochloric acid and dried.

III. Follow the Westenfelder method described by him as follows: "Take a carbon filter tube, put a shallow plug of absorent cotton in the neck and on top a layer of asbestos about 15 mm. thick, gently pack down; on top of this a little kaolin, say one-half gram, rotating the tube so that the kaolin will become equally distributed over the surface and especially to leave some between the walls of the tube and the asbestos. Now put another plug of asbestos on top of this, say 10 mm. thick, also gently packed down, connecting this prepared tube with a long stemmed funnel; wash by pouring dilute HCl, say about 50 cc., in the funnel and follow with say 250 cc. or more of distilled water. When drained pour the tannin in the funnel and discard the first 200 cc. or more of filtrate. Reserve the following filtrate and return if not clear until so. For liquors that have a certain amount of acidity the filtration can be made in a tube having no kaolin and without previous washing with dilute HCl, as the necessary washing is done with the tannin solution itself provided that the asbestos contains no iron; then washing with dilute HCl is necessary. We find that asbestos such as is used by makers of magnesia steam pipe coverings to be the most satisfactory and in fact necessary. It is of a woolly nature and very fibrous. When the tube has been properly packed the filtration proceeds at the rate of one drop per second or three drops in two seconds."

No one of the members was able to obtain satisfactory results by the Westenfelder method and what few results were reported were so widely at variance that it seems unnecessary to tabulate them. Results by the official and the Reed methods follow:

The collaborators comment as follows:

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| | TOTAL SOLS. | | SOLUBLE SOLIDS: OFFICIAL | | | | | | SOLUBLE SOLIDS: ASBESTOS-KAOLIN | | | | | | INSOLUBLES | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | Time | | | | | | Time | | | | | |
| | Weight | Per cent. | Weight | Per cent. | Digest. | Collect. | Total | Char. | Weight | Per cent. | Digest. | Collect. | Total | Char. | Official Per cent. | Asb.-Kal. Per cent. |
| **QUEBRACHO** | | | | | | | | | | | | | | | | |
| Van Gyn.. | 0.257 | 85.8 | 0.235 | 77.7 | 60 m | 150 m | 210 m | Opal | 0.228 | 75.7 | ? | 40 m | ? | Brill | 8.1 | 10.1 |
| | | | 0.231 | | | | | | 0.226 | | | | | | | |
| Oberfell... | 0.5267 | 87.78 | 0.4801 | 79.97 | 75 m | 80 m | 155 m | Opal[1] | 0.4718 | 78.88 | 7 m | 26 m | 33 m | Clear | 7.81 | 8.90 |
| | | | 0.4796 | | | | | | 0.4748 | | | | | | | |
| Reed..... | 0.5276 | 87.93 | 0.4758 | 79.30 | 60 m | 93 m | 153 m | Brill | 0.4762 | 79.36 | 7 m | 35 m | 42 m | Brill | 8.63 | 8.57 |
| Small..... | 0.5234 | 86.95 | 0.4731 | 78.62 | 67 m | 106 m | 173 m | Brill | 0.4728 | 78.62 | 5 m | 25 m | 30 m | Brill | 8.33 | 8.33 |
| | | | 0.4735 | | 67 m | 114 m | 181 m | | 0.4737 | | 5 m | 30 m | 35 | | | |
| **HEMLOCK** | | | | | | | | | | | | | | | | |
| Van Gyn.. | 0.3105 | 44.3 | 0.2775 | 39.65 | 60 | 145 | 205 | Opal | 0.270 | 38.45 | ? | 50 | ? | Clear | 4.65 | 5.85 |
| | | | 0.2780 | | 60 | 140 | 200 | | 0.268 | | ? | 50 | ? | | | |
| Oberfell... | 0.6525 | 46.64 | 0.5717 | 40.85 | 70 | 130 | 200 | Clear | 0.5488 | 39.26 | 6 | 23 | 29 | Clear | 5.79 | 7.38 |
| | | | 0.5714 | | | | | | 0.5498 | | | | | | | |
| Reed ..... | 0.6555 | 46.82 | 0.5650 | 40.36 | 60 | 169 | 229 | Clear | 0.5649 | 40.35 | 8 | 67 | 75 | Brill | 6.46 | 6.47 |
| Small..... | 0.6483 | 46.30 | 0.5615 | 40.15 | 67 | 128 | 195 | Brill | 0.5644 | 40.29 | 13 | 100 | 113 | Brill | 6.15 | 6.01 |
| | | | 0.5630 | | 67 | 123 | 190 | | 0.5640 | | 10 | 80 | 90 | | | |
| **OAK BARK** | | | | | | | | | | | | | | | | |
| Van Gyn.. | 0.345 | 43.1 | 0.339 | 42.28 | 60 | 55 | 115 | Opal | 0.335 | 41.83 | ? | 30 | ? | Brill | 0.82 | 1.27 |
| Oberfell... | 0.7297 | 45.49 | 0.7084 | 44.08 | 70 | 50 | 120 | Clear | 0.6945 | 43.27 | 7 | 15 | 22 | Clear | 1.41 | 2.22 |
| | | | 0.7058 | | | | | | 0.6935 | | | | | | | |
| Reed..... | 0.7176 | 44.85 | 0.6925 | 43.28 | 60 | 67 | 127 | Clear | 0.6940 | 43.38 | 6 | 30 | 36 | Brill | 1.57 | 1.47 |
| Small..... | 0.7193 | 44.91 | 0.6949 | 43.44 | 65 | 66 | 131 | Brill | 0.6948 | 43.33 | 4 | 14 | 18 | Brill | 1.47 | 1.58 |
| | | | 0.6964 | | 64 | 74 | 138 | | 0.6931 | | 4 | 26 | 30 | | | |

[1] Slightly.

Van Gyn evaporated 50 cc. portions instead of 100 cc.

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| | TOTAL SOLS. | | SOLUBLE SOLIDS | | | | | | | | | | | | INSOLUBLES | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | OFFICIAL | | | | | | ASBESTOS-KAOLIN | | | | | | | |
| | | | | | Time | | | | | | Time | | | | | |
| | Weight | Per cent. | Weight | Per cent. | Digest. | Collect. | Total | Char. | Weight | Per cent. | Digest. | Collect. | Total | Char. | Official Per cent. | Asb.-Kal. Per cent. |
| **CHESTNUT WOOD** | | | | | | | | | | | | | | | | |
| Van Gyn.. | 0.336 | 42.0 | 0.329 | 41.05 | 60 | 60 | 120 | Clear | 0.329 | 41.15 | ? | 35 | ? | Brill | .95 | .85 |
| | | | 0.328 | | | | | | 0.330 | | | | | | | |
| Oberfell... | 0.6945 | 43.38 | 0.6874 | 42.95 | 70 | 40 | 110 | Clear | 0.6814 | 42.60 | 4 | 25 | 29 | Clear | .43 | .78 |
| | | | 0.6873 | | | | | | 0.6822 | | | | | | | |
| Reed..... | 0.6908 | 43.18 | 0.6818 | 42.61 | 60 | 45 | 105 | Brill | 0.6817 | 42.61 | 5 | 17 | 22 | Brill | .57 | .57 |
| Small .... | 0.6943 | 43.17 | 0.6821 | 42.41 | 66 | 66 | 132 | Brill | 0.6831 | 42.52 | 4 | 10 | 14 | Brill | .76 | .65 |
| | | | 0.6819 | | 64 | 61 | 125 | | 0.6847 | | 3 | 13 | 16 | | | |
| **STRONG LIQUOR** | | | | | | | | | | | | | | | | |
| Van Gyn.. | 0.318 | 12.72 | 0.310 | 12.40 | 60 | 60 | 120 | Clear | 0.311 | 12.40 | ? | 25 | ? | Clear | .32 | .32 |
| | | | 0.310 | | | | | | 0.309 | | | | | | | |
| Oberfell... | 0.6630 | 13.26 | 0.6482 | 12.95 | 65 | 42 | 107 | Clear | 0.6468 | 12.94 | 5 | 3 | 8 | Clear | .31 | .32 |
| | | | 0.6472 | | | | | | 0.6482 | | | | | | | |
| Reed..... | 0.6643 | 12.59 | 0.6463 | 12.25 | 60 | 50 | 110 | Brill | 0.6468 | 12.26 | 5 | 10 | 15 | Brill | .34 | .33 |
| Small..... | 0.6688 | 12.68 | 0.6529 | 12.38 | 66 | 52 | 118 | Brill | 0.6514 | 12.37 | 3 | 8 | 11 | Brill | .30 | .31 |
| | | | 0.6526 | | 64 | 53 | 117 | | 0.6531 | | 3 | 8 | 11 | | | |

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| | TOTAL SOLS. | | SOLUBLE SOLIDS | | | | | | | | | | | | INSOLUBLES | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | OFFICIAL | | | | | | ASBESTOS-KAOLIN | | | | | | | |
| | | | | | Time | | | | | | Time | | | | Official | Asb.-Kal. |
| | Weight | Per cent. | Weight | Per cent. | Digest. | Collect. | Total | Char. | Weight | Per cent. | Digest. | Collect. | Total | Char. | Per cent. | Per cent. |
| **MEDIUM LIQUOR** | | | | | | | | | | | | | | | | |
| Van Gyn.. | 0.334 | 7.86 | 0.325 | 7.61 | 60 | 75 | 135 | Clear | 0.321 | 7.54 | ? | 25 | ? | Brill | .25 | .32 |
| | | | 0.322 | | | | | | 0.320 | | | | | | | |
| Oberfell... | 0.7067 | 8.31 | 0.6942 | 8.16 | 65 | 55 | 120 | Clear | 0.6905 | 8.12 | 5 | 5 | 10 | Brill | .15 | .19 |
| | | | 0.6932 | | | | | | 0.6896 | | | | | | | |
| Reed..... | 0.6884 | 7.83 | 0.6742 | 7.67 | 60 | 55 | 115 | Brill | 0.6735 | 7.66 | 5 | 14 | 19 | Brill | .16 | .17 |
| Small..... | 0.6858 | 7.81 | 0.6756 | 7.65 | 66 | 85 | 151 | Brill | 0.6756 | 7.69 | 3 | 13 | 16 | Brill | .16 | .12 |
| | | | 0.6687 | | 64 | 73 | 137 | | 0.6763 | | 3 | 10 | 13 | | | |
| **WEAK LIQUOR** | | | | | | | | | | | | | | | | |
| Van Gyn.. | 0.331 | 3.78 | 0.315 | 3.61 | 60 | 140 | 200 | Clear | 0.309 | 3.53 | ? | 40 | ? | Clear | .17 | .25 |
| | | | 0.316 | | | | | | 0.308 | | | | | | | |
| Oberfell... | 0.6939 | 3.97 | 0.6691 | 3.82 | 65 | 100 | 165 | Clear | 0.6654 | 3.80 | 6 | 18 | 24 | Clear | .15 | .17 |
| | | | 0.6680 | | | | | | 0.6655 | | | | | | | |
| Reed..... | 0.7041 | 3.95 | 0.6724 | 3.77 | 60 | 120 | 180 | Clear | 0.6702 | 3.76 | 8 | 50 | 58 | Brill | .18 | .19 |
| Small..... | 0.6984 | 3.92 | 0.6668 | 3.75 | 73 | 156 | 229 | Clear | 0.6645 | 3.72 | 4 | 35 | 39 | Brill | .17 | .20 |
| | | | 0.6680 | | 66 | 167 | 233 | | 0.6622 | | 4 | 38 | 42 | | | |

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Van Gyn:—"I consider Reed's method the best.

1. It works quicker than the other two.

2. It gives perfectly clear filtrates without a trace of opalescence, especially notable in the case of Quebracho and Hemlock. The official method compares in results favorably with those of Reed, but as shown in column 8 the filtrates were sometimes opalescent which was *never* the case with Reed's method. I should like to propose to you to make the following condition in the rules of analysis as regards the filtrate in soluble solids estimation: The filtrate must be clear both by transmitted and reflected light. The Reed method answers completely to this."

Loveland:—"The water pressure we have here is so weak that at no time can I secure more than 14" of vacuum. This too is the exception rather than the rule for the gauge ranges from 4" to 11" the greater part of the time. I cannot secure vacuum enough to draw over 100 cc. portions. While I am discontinuing it for the above reason I would also like to say that I consider the suction method burdensome and tedious and that it would be out of place in any laboratory where real work must be accomplished."

Oberfell:—"One objection in my opinion to method II is the apparent difficulty of manipulation, to say nothing of vacuum pumps and apparatus in laboratories where for example 30 to 40 extracts and liquors are analyzed daily. It seems to me that as the number of analyses or filtrations is increased, the difficulty of proper manipulation would also increase. The above is not my only objection. My results on the samples you sent me are the only data on which I can make any deduction whatsoever, but there were some incongruities there which I would like to investigate further."

Reed:—"I found the apparatus set up as you recommended not entirely satisfactory since a slight difference in the degree of vacuum between the 250 cc. flask and the 500 cc. flask produced a cloudiness through the sudden jerking forward or backward of the filtering solution, when I started to collect my 100 cc. I believe the apparatus should be so arranged that we would not be obliged to collect the filtrate for the determination in any entirely separate vessel so far as the vacuum is concerned. The apparatus as originally described by me did not have this fault.

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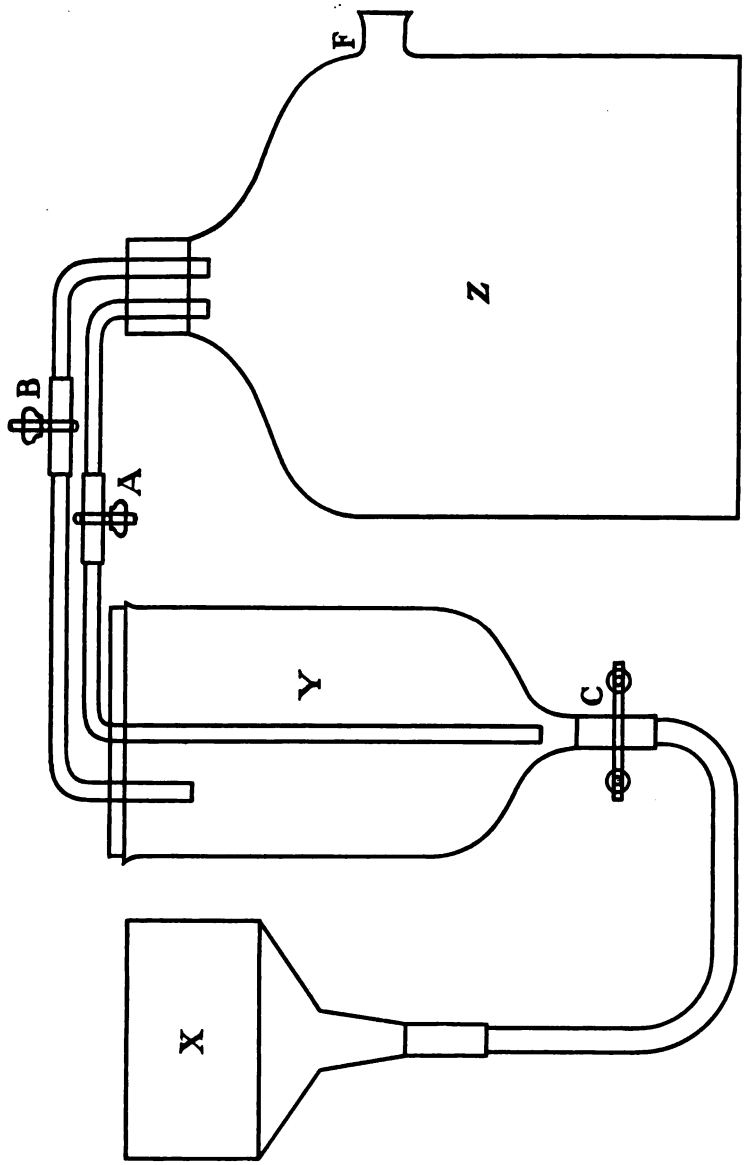
I give you herewith a sketch of another form which I believe to be an improvement on either.




"To start filtration close cock B and open cock A. Tube to

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vacuum pump attached at F. Throw on solution with asbestos at X as directed and suck down firmly. Throw on solution and kaolin and run up vacuum to 16", and run till clear. Close A. and open B, collecting clear filtrate in Y. Close cock C to stop filtration. Filtrate passes over into Z until it comes clear, and when it does the filtrate can be collected with exactly the same vacuum and without any jerking.

"It seems advisable to have the vessel in which we collect the filtrate of greater capacity than 500 cc.; greater, at any rate, for solutions with high insolubles and which filter slowly. With the usually clear solution such as we obtain from a chestnut extract the 500 cc. flask has ample vacuum capacity, but with solutions of hemlock or ordinary quebracho extracts a 750 cc. flask is to be preferred.

As to the question that has been raised relative to the inability of the analyst to accomplish as many filtrations by the proposed method as by the present official method by reason of the impossibility of keeping the funnels filled where filtration goes on at a greatly increased rapidity, I am confident that this can be readily controlled by proper mechanical devices. The apparatus should be fitted with a cock by means of which the filtration can be immediately discontinued at any time, which is provided for in the apparatus you have advised and in the one sketch of which I submit. That the funnels may be kept filled I would recommend either that a special filter-plate funnel be designed with sufficient capacity to hold the necessary amount of solution without refilling, or that the usual form of funnel be used and the solution be fed by means of inverted flasks.

It may be of interest to know that in washing the asbestos free of acid I proceeded almost exactly as in the washing of hide-powder, and found it a very serviceable and effective method as well as rapid. If the asbestos is properly prepared and a modicum of intelligence employed, I fail to see why the method cannot be made of exceeding value. As I have before reported, it has never failed to give me clear filtrates and at a considerable saving of time as compared to the present official method. The extracts that you submitted for trial of the method gave very good filtrates in point of clarity by the official method. With an opalescent filtrate by the paper filtration the corresponding filtrate by the as-

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bestos-kaolin method will be clear, and the difference disclosed in soluble solids figures.

I made an attempt to filter according to the Westenfelder method but abandoned it as I was unable to obtain clear filtrates."

In the light of the results tabulated above, the conclusion seems justifiable that filtrations by the Reed method with asbestos and kaolin give results at least as accurate and concordant as do those made by the official method using S. & S. No. 590 filter paper and kaolin.

In attempting to decide whether it is desirable to adopt the Reed method as official, we must consider the relative disadvantages as well as the advantages of the method. It has been urged against the method that it is impracticable in laboratories where the water pressure is small and variable. Such a condition would certainly render the use of the ordinary water aspirator difficult if not impracticable. It would seem a very simple matter, however to install an air pump run by mechanical power and fitted with a reservoir of suitable capacity whereby the filtration apparatus could be exhausted to the requisite vacuum in short order. This objection relates in fact wholly to a purely mechanical detail which it would seem that ordinary ingenuity would easily provide for in view of the wide range of apparatus manufactured for rarifying air.

It is further urged that it will be difficult to secure suitable asbestos. The several members of the Committee seem with one exception to have met with no difficulty on this score. No asbestos was supplied the members for the collaborative work, each one used his own material and the close agreement obtained would argue strongly that the results by the Reed method are not dependent on the particular sample of asbestos used. Naturally, ordinary care and common sense must be used in selecting or preparing asbestos of a fibre suitable for the purpose in hand and the asbestos must be thoroughly washed with acid to free it from impurities, but with these ordinary precautions no trouble is likely to arise relating to the asbestos.

The only other objection urged against the method, so far as the Chairman knows, is that the apparatus is difficult of manipulation. This objection is the only really valid one and it remains to be seen how serious this objection really is. A modicum of

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experience is required in throwing the asbestos on the filter plate so as to secure a satisfactory mat, but this certainly is no serious objection. The original apparatus suggested by Reed (JOURNAL, A. L. C. A., Vol. II., p. 421) was too fragile and costly for general use. The apparatus devised by the Chairman and suggested by him for the collaborative work of the Committee was an improvement, but was open to the objection made by Mr. Reed that when changing the collection from one flask to the other a difference in the degree of vacuum in the new flask by causing a change of pressure on the mat might produce a temporary cloud in the filtrate. The Chairman by using some care in opening the pinch cocks used had no trouble of this sort, but the apparatus did unquestionably require care in this particular and in so far was defective for general use. The last apparatus devised by Reed is probably an improvement on either of the other two. The Chairman unfortunately has been unable thus far to put it into practical use and so convince himself of its merits or otherwise, and whether it is the last word is open to question.

The Chairman fully and confidently believes that it is entirely possible to devise an apparatus which will be so simple and automatic in its action that it will require less attention from the operator than the official method with filter paper. Whether Reed in this last apparatus has achieved this, only practical experience can tell, but the apparatus certainly looks promising. Where only a few analyses have to be made the Reed method certainly means a marked saving of time and attention as shown by the tabulated results.

As against these disadvantages, real or otherwise, of the Reed method we have the positive advantages that first there is a marked saving of time as regards individual filtrations; second there is less absorption of tannin in the process of filtration than when the official method is used; third the filtrates obtained are almost invariably brilliantly clear when observed either by transmitted or reflected light, a result not always obtainable by the official method.

While a majority of the Committee are in favor of the Reed method the number of those who actually did the work is so small and the work accomplished is so indecisive as regards the practicability of the method when used in a large way that the

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Chairman feels some hesitancy about recommending the adoption of this method at the present time. Personally, he is fully convinced that the method has decided advantages over the present official method and that its adoption should be merely a question of time depending upon the finding of a satisfactory form of apparatus. He would therefore recommend that the Reed method be tried out in a larger way during the coming year to the end that it may be adopted at least as an alternative method for soluble solids filtration at the annual meeting of 1909.

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## STANDARDIZATION OF HIDE-POWDER.

*By Dr. J. Gordon Parker and Alex. T. Hough.*

The lines taken up by the authors in this paper have been governed by a factor recognized by Bennett in his paper on the "Standardization of Hide-powder," which we herewith quote:

"The fact that granular powders give higher non-tannins and still absorb all the tannin is a point from which it may be argued that granular powders are better. From the standpoint of the approximation to the true value of tanning matters in an extract, this is no doubt true, and has already been claimed as a virtue for the Buffalo hide-powder."

"At the same time, the writer recognizes that most powders in use for the shake method have a more fibrous texture, such as, for example, that used by the American Leather Chemists Association, and thinks, therefore, that here truth may be sacrificed for sake of general concordance."

Another governing factor has also been, that the trade has already been much confused by the introduction of the new method, through their inability to correctly interpret the portent of the changed figures obtained by it, and if at this juncture, when they are just getting used to the changed condition, another change of figures was effected, a much greater and very unwelcome confusion would result, and the trade would be up in arms against the chemist for his instability.

The greater majority of the members of the I. A. L. T. C. have been, during the past few months, making their analyses by means of Dr. Paessler's hide-powder, and no doubt they have all experienced the practical difficulties of washing this powder, es-

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pecially towards the end of the operation, when the powder assumed a more or less gelatinous condition which renders it very difficult to squeeze, and more often than not the cloth is broken when the absolutely necessary operation of squeezing in the press is resorted to.

Another objection to this powder is that it is very soluble in cold water, as would be expected from its condition, and that as moisture is always determined by the Procter-Bennett method, on the assumption that no matter is washed out, this soluble matter is replaced by and calculated as moisture, thereby causing at any rate a theoretical error, although its proportion might not be sufficient to make it a practical one.

Having, as mentioned before, recognized the fact that changed figures (which any other powder would certainly give) are undesirable, the authors have adopted Paessler's powder, which, apart from its difficult manipulation, gives good results, as standard, and have attempted successfully the adaption of the powder used by the A. L. C. A. to the requirements of the I. A. L. T. C.

The first experiments were carried out with an almost neutral powder, side by side with Paessler's powder, so that comparable results might be obtained. In all following experiments the powder worked with was always more acid than that used in the previous experiment, the increase being continued until a point was reached where the results obtained by the American powder were identical with those obtained by means of Paessler's. At this point the American powder had an acidity of 5°.[1]

The results of these experiments are seen in the tables. Nos. 1 and 4 are the columns to which the authors would draw special attention, No. 1 being the results by the official method, using Paessler's powder, and No. 4 being those obtained by means of American powder after reducing to an acidity of 5°.[2] It will be noted that in almost every case the results agree well within the bounds of experimental error. The only peculiarity is the case of Mimosa D. This heavily sulphited extract yields rather inconclusive results, and experiments are being continued with it with a view to explaining its peculiar behavior. Interesting re-

[1] "Standardization of Hide Powder." Bennett, "Collegium," No. 254, 1907.

[2] "Standardization of Hide Powder." Bennett, "Collegium."

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sults are also being obtained with Freiberg and Vienna powders, and it is hoped that these will soon be ready for publication.

The exact procedure adopted in standardizing the American powder is as follows:

Sufficient powder is weighed into an agitation flask for the work in hand, to equal 6.5 grams dry hide per analysis, acidity 8° (this being the natural acidity of the American powder); ten times the weight of powder, in water, is then measured out, and such a quantity of N/10 NaOH is added as will reduce the bulk of the hide-powder to an acidity of 5° (in this case 3 cc. per 6.5 gram dry hide) after mixing; the solution is poured on the powder and the whole agitated for 20 minutes, when the required quantity of 10 per cent basic chrome chloride is added directly to the powder, stirring all the time, and the whole is agitated for one hour and proceeded with as usual.

It has been suggested that a specific acidity should be insisted upon in the rules, but this course is impossible unless all chemists are working with an absolutely identical powder. For, as will be seen in the tables, it would not be possible to obtain concordant results by identifying the acidity of Paessler's powder with that of the American, and therefore the above method of stan-

| Extract | Paessler's powder used as per official method | American powder rendered 10.0 acid by chroming 20 minutes with 2 cc. N/10 HCl per 6.5 grams dry hide | American powder rendered 6.5 acid by chroming 20 minutes with 1.5 cc. N/10 NaOH per 6.5 grs. dry hide. | Ditto Acidity 5.0 | Ditto Acidity 3.5 | Ditto acidity 2.0 | Ditto alkalinity 2.0 |
|---|---|---|---|---|---|---|---|
| Chestnut..... | .0450 | .0410 | .0440 | .0450 | .0460 | .0470 | .0580 |
| Oakwood..... | .0865 | .0830 | .0840 | .0860 | .0870 | .0890 | .0990 |
| Quebracho..... | .0210 | .0260 | .0200 | .0210 | .0210 | .0220 | .0290 |
| Hemlock..... | .0730 | .0780 | .0680 | .0720 | .0730 | .0750 | .0830 |
| Mimosa D(LDG) | .0610 | .0570 | .0580 | .0590 | .0580 | .0630 | .0640 |
| Mangrove..... | .0510 | .0560 | .0500 | .0510 | .0530 | .0530 | .0540 |
| Hemlock decolorized..... | .1010 | — | .1000 | .1000 | .1010 | .1020 | .1040 |

dardization is suggested as the way out of the difficulty. Some discussion took place at the meeting of the British Section of the

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Association on March 21st as to the validity of this method of modifying the acidity of hide-powders, and ultimately it was proposed by Mr. Bennett "that the method of adjusting the acidity of the hide-powder immediately prior to analysis was within the rules of the I. A. L. T. C." This was seconded by Mr. Wood and carried unanimously.

Therefore, in view of obviating the errors and difficulties attending the use of Dr. Paessler's hide-powder, the authors recommend that some more granular powder be used, such as American or Vienna, and be standardized, if necessary, immediately prior to analysis by their method.—*Collegium.*

Editorial Note:—The practice of reducing the acidity of hide-powder by the addition of alkali to the wet powder before chroming, has obtained among American chemists for some years.

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## PRELIMINARY REPORT OF THE COMMITTEE ON THE ANALYSIS OF FATS AND OILS.

*By F. W. Alden.*

Early in 1907 a committee was appointed to investigate the question of the analysis of fats and oils used in the manufacture of leather, and report, what, in their judgment, were the best methods for testing these materials. The committee was small at the outset, but as some of the members were unable to serve, there finally remained but three including the chairman.

The work of last year was reported to the Association and appeared in the September and October numbers of the JOURNAL, pages 285 and 359. The chairman tried to make it a sort of composite report, including the ideas of all the members of the committee. There was, however, one phase of the subject omitted and concerning a matter upon which there had been as much deliberation as anything else. It was a method for the analysis of Sod Oil and Moellon. One of the first things done by the chairman was to submit quite lengthy suggestions on the subject. In fact a method for the complete analysis was proposed and carefully gone over by each member of the committee. The reason it was not presented to the Association was, that towards the last, additional information was received which made it seem best

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to consider the matter more in detail later on, when more time could be given to it and not over burden an already somewhat voluminous report. And now since the same committee has been reappointed for the year 1908, there seemed to be nothing better than that we should confine ourselves to the matter which had been left over from last year, and try to make a somewhat full report on this very important question.

Accordingly the chairman again submitted a method to his committee, entirely rewritten and revised containing some improvements of his own, and following the lines of the report of the French Commission which appeared in the *Collegium* in 1906. This Commission of which M. F. Jean was president, covered the ground very well, although their report seems to be somewhat lacking in detail. With this before him, the chairman drew up a detailed method for the analysis of Sod Oil and Moellon, and submitted it to his committee together with samples, requesting them to make as many of the determinations as possible. It should be said in this connection that the committee this year has been assisted by Mr. A. G. Stillwell, at the request of the chairman.

The method, as given to the committee is substantially as follows:

**Tentative Methods for the Analysis of Sod Oil and Moellon.**

*Committee of 1908.*

*Reagents Required.*

Petroleum Ether, boiling below 80° C.

Sulphuric Ether, pure.

Phenolphthalein Indicator, one gram dissolved in 100 cc. of alcohol.

Alcohol, ordinary grain alcohol, 95% by volume.

Purified Alcohol, prepared as directed on page 23 of the 1908 Manual under, "Provisional Methods for the analysis of Oils and Fats."

Half Normal Alcoholic KOH. *Loc. cit.*

Aqueous KOH solution, 50% by volume, prepared by dissolving 50 grams of pure stick potash in sufficient water to make 100 cc. of solution.

Dilute Acetic Acid Solution, 25% by volume. Made by dis-

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solving 25 grams 95.5% acetic acid in sufficient water to make 100 cc. of solution.

Strong hydrochloric acid. C. P. acid of 1.19 sp. gr.

Standard iodine solution. Hanus iodine solution, *loc. cit.*, p. 24.

### *Statement of Results.*

The following percentages should be calculated on the basis of the moisture free weight of the oil: Moisture, ash, impurities, free fatty acids, total unsaponifiable matter, total oxidized fatty acids, total unoxidized fatty matter.

### *The Analysis.*

### *Moisture.*

*Procedure* 1. Fahrion's Method—By the direct application of a flame. Weigh off accurately between 2 and 3 grams of oil in a tared platinum crucible. Place on a porcelain triangle in an inclined position and heat gently with a low flame, held a short distance below. When ebullition ceases and smoke is seen passing off from the oil, the water is supposed to have been all driven off. This is sometimes indicated by a crackling sound in the oil. After cooling the oil by placing on a block of iron or stone, reweigh. The loss in weight is the moisture.

*Procedure* 2. Moisture driven off by long continued drying. The Sand Method. Take a porcelain crucible cover about 65 mm. in diameter and break off the handle. File the broken place down smooth and use as a dish in which to dry the oil. This makes a dish of convenient size and shape, although any flat-bottomed dish of about such a diameter will answer just as well. Cover the bottom with clean quartz sand previously washed with hydrochloric acid and distilled water to a depth of about $^3/_{16}$ of an inch, and place in a drying oven. After drying and cooling, weigh for tare and then add the required amount of oil. This should preferably be done late in the afternoon and the drying be allowed to continue over night. After from 14 to 16 hours drying the loss in weight is determined and calculated as moisture.

*Note* 1. There should always be less oil used than the sand will absorb. When the oil is heated it works its way along the bottom of the dish, leaving dry sand above which forms a sort of protection for the oil against oxidation by the air.

*Note* 2. A time limit must necessarily be prescribed since dry-

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ing to constant weight has been proved impossible by the writer (see JOURNAL A. L. C. A., Vol. II, p. 12).

*Ash.*

If procedure 1 has been used for the determination of moisture the residue may be burned directly by applying a flame. Otherwise it is necessary to first drive off the water after which the oil should be allowed to burn slowly until consumed and then the residue heated to a dull redness until all the carbon has been burned away and the residue weighed as ash.

*Examination of the Ash.*

There should not be more than a very small amount of iron present. If the appearance of the ash indicates a considerable quantity it is well to estimate the amount. If the ash shows a tendency to fuse, add water, filter, and titrate the sodium carbonate with standard acid.

*Impurities.*

Weigh off 10 grams of the oil and place in an oven until the water has been expelled. Then add a quantity of petroleum ether and stir together with a glass rod. Then pour the petroleum ether solution on a tared filter, washing the insoluble matter on to the filter with more petroleum ether and continue the washing until all soluble matter has passed through. Finally wash with sulphuric ether and after drying weigh the residue.

Note.—The filtrate is reserved for another determination.

*Free Fatty Acids.*

Take the filtrate from the separation of the impurities and distill off the petroleum ether and also the sulphuric ether. In the meantime take about 30 cc. of alcohol and add one cc. of one per cent. phenolphthalein and render slightly pink by the addition of sufficient alcoholic KOH. After heating the alcohol, add it to the oil and titrate the acidity with the alcoholic potash. The result is to be expressed in terms of oleic acid.

*Total Unsaponifiable Matter.*

*Procedure* 1. Weigh off about 6 grams of the oil into a digestion flask provided with a condenser or long glass tube. Add as many cc. of the 50 per cent. aqueous KOH as grams of the oil

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taken, and 25 cc. of ordinary alcohol. Heat on the water bath, with frequent agitation, especially at the beginning of the operation, so as to get the contents in solution as much as possible. After digesting for one hour, cool and transfer to a 16 oz. separatory funnel. Rinse the flask with a little distilled water a few times, adding the rinsings to the soap solution. Then add about 75 cc. of sulphuric ether and stopper the funnel. Lay the funnel on its side and roll back and forth for several minutes, at first slowly until it is seen how much agitation the mixture can endure without forming an emulsion. Then draw off the soap and rinse the ether with small quantities of distilled water adding the rinsings to the soap solution. The funnel is then again stoppered, after the addition of more ether, and the process of shaking out repeated. This should be done a third, or even a fourth time, excepting that the washings may not be added to the soap solution after the 2d or 3d shaking outs. After the various ether portions have been well washed, they are filtered into a tared flask and the solvent distilled off. The last traces of moisture and ether may be removed by passing a current of air through the flask with subsequent drying in an oven for four hours. The flask is then cooled and weighed.

*Procedure 2.* Saponify in the same manner as in procedure 1, but pour the soap solution into an evaporating dish instead of a separating funnel and rinse the flask with alcohol instead of distilled water. The dish containing the soap is then placed on the water bath, and when most of the alcohol has passed off, add 25 grams of clean quartz sand previously washed with hydrochloric acid and distilled water. Stir the mass occasionally with a glass rod, and when it appears to be perfectly dry, which may be accomplished in from 16 to 20 hours, pulverize in a mortar and place in a Soxhlet extractor, and extract continuously for at least 4 or 5 hours. At the end of that time filter the petroleum solution into a separatory funnel, and wash 2 or 3 times with distilled water. The ether is then transferred to a tared flask, the solvent distilled off in the same manner as in procedure 1, and the contents weighed.

*Note.*—In the presence of difficultly saponifiable fats like Wool Grease, the two methods of saponification may yield widely different results, since procedure 1 will not completely saponify the

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fat. The long continued drying in the oven of procedure 2, however, seems to be much more effective in breaking up the alcoholates of which Wool Grease is so largely composed.

*Total Oxidized Fatty Acids.*

*(Degras Former).*

The following method depends upon the principle that the oxidized fatty acids are insoluble in petroleum ether, while the unoxidized are soluble. The mixed glycerides must therefore be saponified and the fatty acids liberated by acidifying the aqueous soap solution. Here it is found that a considerable part of the degras former is soluble in water and to regain this, repeated evaporations are resorted to.

Weigh accurately into a suitable flask 8 or 9 grams of the oil and saponify in the same manner as in the determination of unsaponifiable matter, Procedure 1, excepting that purified alcohol is used and the saponification continued for only 20 minutes instead of one hour. Then cool under a tap and use a little distilled water to rinse the flask. Acidify with a slight excess of the 25 per cent. acetic acid solution, about 23 cc., and again cool if necessary. About 75 cc. of petroleum ether is then added and the mixture gently agitated; the aqueous part is drawn off into another separatory funnel, the petroleum washed twice with small amounts of distilled water and the washings added to the aqueous portion. Another quantity of about 75 cc. of petroleum ether is then added and the mixture shaken quite violently. The aqueous part will then separate out clear and may then be drawn off into a large flat-bottomed porcelain evaporating dish. The contents of the separatory funnel are washed with small amounts of distilled water and the washings added to the evaporating dish. This will probably cause precipitation, but that does not matter since all of the unoxidized matter has been removed. The dish is then placed on the water bath and attention turned to the contents of the two separatory funnels which contain not only the unoxidized fatty matter but also most of the Degras Former or resinous matter, as it may be called. Pour off the petroleum ether into a 200 cc. graduated flask, using more petroleum to rinse and thoroughly wash the resinous matter. Finally make up to the mark and set aside for the time being. When the aqueous part, containing considerable degras former in solution, has evaporated

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down to a few cc., 10 cc. of strong hydrochloric acid is added and the heating continued a few minutes longer. The black resinous matter, which has, by this treatment, become quite insoluble, is then washed with distilled water and the washings evaporated down nearly to dryness. It will then be seen that more resinous matter has become insoluble and that is also filtered off and washed in the same manner as the first case. (A cotton plug is the most convenient form of filter in these cases). After the washings have been nearly evaporated off the second time pour the small quantity of solution still remaining into another evaporating dish and continue the drying of both dishes for half an hour. At the end of this time wash the resinous matter as before. These various portions of degras former are then to be collected by dissolving them in alcohol and filtering the alcoholic solution through paper into a tared dish of some kind, and after evaporating off the solvent, the residue is dried in the oven for 4 hours and weighed. Although the degras former dissolves slowly, it is nevertheless all soluble in a comparatively small quantity of alcohol.

It sometimes happens that a precipitate forms in the alcoholic solution. It should then be filtered a second time when it will probably remain clear. The dried residue is the Degras Former.

*Note.*—The chairman has introduced various modifications in the above method in order to reduce the amount of oxidation to a minimum during the process of analysis. It being necessary to evaporate down the aqueous part after breaking up the soap solution, it was found that this could be done in comparative safety if the use of strong mineral acid was avoided. But acetic acid does not seem to be able to completely precipitate the oxidized fatty acid and for that reason hydrochloric acid is added later when the solution has been reduced to a small bulk. The degras former can then be exposed to the action of the HCl in the heat for a short time without danger, that is, long enough to completely precipitate the oxidized fatty acids.

### *Total Unoxidized Fatty Matter.*

### *(Fatty Acids and Unsaponifiable Matter.)*

The petroleum ether of the preceding determination should preferably be allowed to stand over night in order to settle out or clear, or it may be clarified by filtering at once, provided the

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evaporation is not sufficient to materially decrease the volume. The resinous matter thus obtained should of course be added to the other portions. Ten cc. of the clear solution are now drawn off into a 16 oz. glass stoppered bottle and set aside for iodine value. The pipette is then rinsed back into the main petroleum ether solution. The latter is then transferred to a tared flask the solvent distilled off, the last portions being removed by means of a current of air and four hours drying in the oven, and the residue weighed. After correcting for the amount taken out for the iodine value the amount of unoxidized fatty matter is thus obtained.

*Iodine Value of the Unoxidized Fatty Matter*

The petroleum ether of the 10 cc. set aside for this purpose is removed in the following manner: Fit a rubber or cork stopper into the mouth of the bottle. The stopper should have two perforations through one of which a glass tube is passed to within an inch of the bottom of the bottle. The bottle is then held in water of about boiling temperature and the tube connected with a $CO_2$ generator. Allow a stream of the gas to pass through the bottle while the vapors are being expelled. It is thus seen that the petroleum ether is driven off in an atmosphere of carbonic acid gas, which of course is to avoid oxidation of the oil. The iodine value is then obtained in the regular manner with the Hanus Iodine Bromide solution. The use of chloroform is not necessary if sufficient care be taken in getting the fatty matter completely dissolved in the acetic acid solution. The weight of fat taken for this determination being an aliquot part of the total unoxidized fatty matter the amount is calculated from the weight of the residue obtained in that determination.

*Note.*—Lest the amount taken for iodine value as prescribed above be found on trial to be too much for 25 cc. of the iodine bromide, it is well to be prepared to run a second determination when the correct quantities can be used. For this purpose the flask of petroleum ether solution should be again stoppered after drawing off the portion for iodine value, and set aside until the result of the titration is obtained.

*Melting Temperature of the Unoxidized Fatty Matter*

This is to be obtained according to the method for melting

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point described among the provisional methods for oils and fats of our Association.

*Note.*—The following three points are to be registered: The point at which the fat begins to flow; the point at which the first drop falls; and the point at which the fat becomes entirely melted. The first point is quite indefinite and will probably be found the most satisfactory if taken at the point at which the fat is actually seen to be flowing out of the tube, which will be just before the first drop falls. The three points may be briefly recorded as, *flow, drip, clear.*

It is very important to notice the consistency of the fat when emptying it out of the tube in a melted condition. If it is not perfectly thin and fluid but flows somewhat lazily out of the tube, the fact should be noted.

(To be continued)

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## THE INTERNATIONAL COMMISSION OF THE I. A. L. T. C.

*Circular sent to members by Dr. H. R. Procter, Chairman.*

While in many laboratories the present official process has been found rapid and convenient, and its results much more concordant than those of the old official method, in others the trouble of washing is complained of, and discordant non-tannins results are obtained. As it may be assumed that in all cases the intention is strictly to follow the prescription, it is necessary to ask what are the causes of errors and how they can be prevented.

1. Hide-powder. It is undeniable that slight variations may be due to differences of texture which can hardly be avoided even by the employment of one make only, but which in the writer's experience are unimportant between powders of fairly woolly texture.

More serious than mechanical differences of texture are the structural changes produced by over-liming or unsatisfactory chemical preparation, which make the powder very sensitive to acid swelling in chroming. This defect is pronounced in the white powder of the Freiberg Versuchsanstalt, which is at present used in England, and leads to considerable difficulties in washing and squeezing, though with careful treatment accurate analytical results are obtained. An American powder which has been ex-

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perimentally used is much easier to wash and squeeze and gives good analytical results, but contains acid equal to 8.4 cc. N/10 for 6½ grams which is beyond the limit allowed by the prescription. The effect of excess of acid is usually to increase the absorptive power of the powder, though this is dependent both on the extent of the excess and on the character of the extract, and especially its content of alkaline tannates. As the actual acidity or alkalinity of a powder is easily determined, it would seem desirable to adopt a suggestion of Dr. J. G. Parker's and to correct the powder to absolute neutrality or a determined acidity by addition of standard acid or alkali to the water before chroming. This undoubtedly increases the concordance between results with different powders, and facilitates their manufacture, by diminishing the need for an exact acid content.

2. Chroming. In this operation it is hardly possible for any error to occur, if pure chemicals are used, and carefully weighed out. It has been noted that the prescribed stock solution changes color slightly on keeping, but careful experiments in this laboratory show no difference in absorbency between powders chromed with 6 months old solution, and with that prepared immediately before use, the average of 8 determinations of various extracts each way only showing a difference of 0.03 per cent.

3. The washing is probably the operation in which errors most easily arise. If the chroming has been properly done, the only soluble matters in the liquor are the sodium chloride formed in neutralizing the chrome chloride, and a minute trace of chromium as basic chloride amounting to about 0.005 per cent. on the chroming liquor and 0.05 per cent. on the dry powder used. The common salt on the other hand is not perceptibly absorbed by hide, and amounts in all to 0.066 per cent. on the liquor and 0.66 per cent. on the powder. As 6½ grams of powder properly squeezed contain under 20 cc. of liquor, and only half of this is contained in the 60 cc. of detannized solution evaporated, the total weight of dissolved salts in the latter amounts to only 6.6 mgr. of NaCl, and 0.3 mgr. Cr. Actual determination of total residue in blank experiments with distilled water on squeezed but unwashed chrome powder gave 7.4 and 8 mgr. respectively including chrome salt and dissolved hide-substance. This on an ordinary 30 per cent. extract would cause an error of under 1 per cent.,

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and insufficient washing cannot therefore be the cause of the considerable errors complained of. The small amount of this error suggests a method of dispensing with washing altogether, which will be referred to later.

A greater danger than that of insufficient washing is that of very slow and protracted washing, or still more, of keeping the chromed powder for more than a few hours before use, since some sort of decomposition sets in which leads to a marked increase in solubles. It is best in every case to chrome only the amount of powder required for immediate use, and to proceed at once to detannization.

The method of washing adopted in the writer's laboratory is to collect the powder after chroming on a suitable linen cloth placed on a funnel, and after squeezing by hand to place in a small screw fruit press and squeeze to about 75 per cent. moisture. The powder is then returned to the shaker jar or to a beaker, with say 10 times its weight of distilled water, in which it is thoroughly broken up either by violent agitation or with a stirring rod. It is then allowed to stand say 15 minutes for diffusion to take place, and the pressing repeated in the same cloth and so on till the requisite freedom from chlorides is attained, which is accomplished in about 4 to 5 pressings at most. The soluble residue of 50 cc. of a blank with distilled water is always below 1 mgr. and usually below 0.1 mgr.

4. Detannization. The only special precaution necessary is to ensure the thorough breaking up of clots of the powder, which is not always easy with a powder which swells so readily as that of Dr. Paessler, but gives no trouble with American powder. The same remarks apply to the subsequent squeezings and filtration of the detannized liquor. Dr. Paessler's powder gives much finely divided colloidal hide-substance, which can only be removed by shaking with kaolin and repeated and careful filtration. Like the tannin solution, the non-tannin solution must be optically clear and free from opalescence, and neglect in this respect necessarily leads to inaccurate results. The really clear solution is generally free from color, and at most a pale yellow.

5. Drying of residues. English experience has condemned the combined evaporator and dryer as only suitable for works control, since the slow evaporation leads to increased oxidation

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with many materials. Probably the best method is evaporation on the water bath in a current of air, and subsequent drying for one hour in the vacuum oven, cooling and weighing and then drying for an additional hour, when the weight should be within 0.001 gram of the previous weighing. If not the drying must be continued for another half hour. Next to the vacuum dryer, a steam or water oven of Moeslinger pattern is to be recommended, about double the above times being required. In the opinion of the writer air ovens should be prohibited, as though probably superior to the water oven in very careful hands, they easily lead to error by over-heating.

Platinum or silver basins are no doubt best, aluminium and nickel not very satisfactory, and well glazed porcelain of flat form probably superior to glass, though Jena glass is no doubt permissible. Great care is required to ensure complete cooling, which is best done in small exsiccators not holding more than two basins and with ground covers which should fit so tightly as to show a partial vacuum when cold. At least 30 minutes is required for uniform cooling. Care must be taken to avoid electrification of the basins caused by rubbing with dry cloths (Cp. Bornemann, *Ch. Zeitung*, 1908, p. 125), which affects the apparent weight. Cl determination in the non-tannin residues is a useful check, but regard must be had to the frequent presence of chlorides in the extracts.

It has been pointed out by Jedlicka (*Colleg.*, 1908, p. 18) that the amount of Cr contained in the official chrome chloride solution only reaches 0.39 gram as a maximum for 100 grams of powder, while the general directions prescribe a chroming of 0.5 to 2.0 gram. The writer must take responsibility for this oversight (*Colleg.*, 1908, p. 51). Jedlicka suggests increasing the chroming of the official powder, as rendering the results more concordant, but as excellent concordance can be obtained by the present prescription if properly carried out, and increased chroming leads to somewhat increased absorption of non-tannins, and more laborious washing, the writer advocates lowering of the general limit to 0.1 to 1.0 per cent. which more closely corresponds with actual European and American practice. This matter must be considered by the Commission but small variations in chroming have but little influence on results.

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The following lines of experimental work are suggested.

(a) Chroming. Comparative experiments with the official prescription and with a double amount of the standard chrome liquor prescribed.

(b) Washing. Any improvements on the method described above. Duplicate blanks should be made with distilled water precisely as in a tannin determination, and chlorides should be determined in the dried residues.

(c) Powders. Comparative tests should be made with any powders available, both as to blanks and tannin absorption. The original moisture and acidity of powder and its physical characters should be noted, and the effect of correction to neutrality by the addition of a calculated volume of standard acid or alkali should be studied. Experiments as to the effect of addition of small known quantities of acid are also desirable.

(d) Suggestion for modified method. The powder is soaked and washed with 10 volumes of water to which the calculated acid or alkali is added for 30 minutes (or upwards). The powder is drained and squeezed into a graduated glass, the volume of expelled liquid is noted, and replaced by an equal volume of water to which the chroming solution is added as prescribed and the chroming is conducted as usual. The chromed powder is squeezed to under 75 per cent. of moisture and weighed and used at once and without washing for detannization, a portion of the squeezed liquid being added instead of distilled water to complete the exact volume. In calculating results a constant correction which will amount to about 7.5 mgr. per 50 cc. but which must be more exactly determined experimentally, is deducted for the solubles in the chroming solution retained by the powder.

The advantages aimed at by this modification are not merely considerable saving of time and trouble, and avoidance of personal error in washing, but greater scientific accuracy of results, since the hydrolysis which takes place in washing is necessarily of an uncertain character, while under the modified method the conditions are always constant and exactly prescribed.

(e) Detannization. Some advantage in facility of clear filtration has been found in adding the prescribed kaolin before instead of after shaking. Comparative experiments should be

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made. Care should be taken that the kaolin used is free from solubles.

(f) Evaporation and Drying. Experiments on the points mentioned under this head are desirable.

Note. No hide-powders are supplied, as it is desirable that these available for the experimenter should be tested; but the writer will be glad so far as possible to send samples of any special powder desired.

No standard extracts are sent, as the question of complete adsorption of tannins may be regarded as settled, and that of concordance between different experimenters is too largely a personal factor to form a useful subject for collaborative work.

No suggestions are made as to the filtration of "total solubles," but the problem cannot be regarded as finally solved.

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## CURRENT ARTICLES.

*A record of contemporaneous technical articles of interest to the tanner and leather chemist.*

*Shoe and Leather Reporter.*

ORIGIN AND METHODS OF PREPARATION OF CHEMICAL SALTS USED IN TANNING. *Anon.*, (concluded) June 11.

FINE DULL FINISHES FOR COLORED CHROME LEATHER. *Anon.*, June 18th.

PRACTICAL SUGGESTIONS FOR THE TANNERY. *Anon.*, Jnne, 11 June 18, June 25, July 2.

CHIEF OBJECT IN ROLLER LEATHER. *Anon.*, June 25.

*Hide and Leather.*

TO COLOR CHROME-TANNED CALFSKINS A DEEP BLACK. *Anon.*, June 13.

CHROME-COLORED CALFSKINS. *Anon.*, June 20, 27.

THE ADDING MACHINE IN THE TANNERY. *Anon.*, June 20.

MANUFACTURE OF BAG, STRAP AND CASE LEATHERS. *Anon.*, July 4th.

CHROME STORM BOOT GRAIN. *Anon.*, July 4th.

DRYING LEATHER. *Anon.*, July 4th.

COLORING OR DYEING LEATHER. *Anon.*, July 11th.

FORMIC ACID IN TANNING. *Anon.*, July 11th.

*The Plant World*, Tucson, Arizona.

CACTUS LEATHER. *F. C. Wright*, May.

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*The Leather Manufacturer.*

USE OF ANILINE COLORS FOR LEATHER. *Anon.*, June.
TANNING FUR AND HAIR SKINS. *Anon.*, June.
MOCHA CASTOR GROVE LEATHER. *Anon.*, June.
STUFFING AND FINISHING HARNESS LEATHER. *Anon.*, June.
OILING CHROME LEATHER. *Anon.*, June.
SOME FACTS ABOUT COAL. *E. G. Bailey.* Current.

*Collegium.*

THE SCIENCE OF THE TANNING PROCESS. *Herzog and Adler.* concluded, (German). June 6.
THEORETICAL STUDIES ON TANNAGE WITH ORGANIC COMPOUNDS. *Meunier and Seyewetz.* (French). June 13 and 20.

*Der Ledermarkt.*

TREATMENT OF CHROME SKINS WITH INFERIOR DRESSING. *Anon.*, June 10.

*Chemiker-Zeitung.*

THE POISONING OF WORKMEN BY CHROMIUM COMPOUNDS. *Prof. Lewin*, June.

*Duetsche Gerber Zeitung.*

THE AMMONIUM CONTENT OF LIME LIQUORS. *Victor Arnstein*, June 4 and 6.

*Der Gerber.*

REMARKS ON A TAN EXTRACT CASE, (LEGAL). *W. Eitner*, June 1. (Suit described May 15).
ON THE HISTORY OF INDUSTRIAL EDUCATION (includes tanning), *Anon.*, June 15th.

*Le Cuir.*

THE FRENCH TANNING SCHOOL. *Editorial*, (Current) June 15.
MEETING OF THE FRENCH SECTION OF THE I. A. L. T. C.
THE MANUFACTURE OF ARTIFICIAL DEGRAS. *U. J. Thuau*, (Current) June 15.
FRAUDULENT WEIGHTING OF HIDES. *Anon.*, (Current) June 15.

*Manchester, Liverpool and District Tanners' Federation, Year Book 1908.*

AMERICAN METHODS OF TANNING. *Dr. J. G. Parker.*
THE OLD AND NEW METHODS OF ANALYSIS. *A. T. Hough.*
BLEACHING OF LEATHER. *M. C. Lamb.*
ANTHRAX. *B. A. Whitelegge.*
DISINFECTION OF HIDES AND SKINS. *Alfred Seymour-Jones.*

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ENGLISH vs. AMERICAN AND CANADIAN SOLE LEATHERS. *Dr. J. G. Parker.*
LEATHER MANUFACTURE IN HOLLAND. *J. L. van Gyn.*
INFLUENCE OF TIME AND MOISTURE UPON LEATHER. *R. A. Earp.*

## REVIEWS

**Study of Tannins.** L. E. CAVAZZA. *Chem. Zentr.*, 1908, 1, 1648-1649.—The author recommends the exclusion of oxygen in the extraction of tannins. This is accomplished by using distilled water, free from oxygen and ammonia, either *in vacuo* or in presence of some inert gas. By so doing, ampelotannic acid may be obtained as fine micaceous leaflets, which, upon evaporation of solution, are formed into ruby-red lamellæ by the action of the air. The author prepared tannates of thallium, caesium, rubidium, strontium, vanadium, thorium, cobalt, nickel, uranium and arsenic, and double tannates of selenium and potassium and of cobalt and potassium. By repeated evaporation in an inert gas, the purified tannin may be obtained, the crystals being removed as formed. For the micro-chemical detection of tannins, thallium carbonate and uranyl nitrate are suitable reagents. Chestnut-tannin is straw-yellow with the former, and rusty-brown with the latter reagent. Other tannins react as follows: Coffee tannic acid, emerald-green coloration or brown precipitate; geranium-tannin, a hyaline or a yellowish-red precipitate; oak-tannin, a cheese-like precipitate or a yellowish-brown solution with slight red precipitate; gallotannic acid, a dark yellow solution with slight red precipitate, or a colorless precipitate; ampelotannic acid, a brown precipitate or a brick-red coloration. Vanadium chloride is especially suitable for the detection of tannins in plants, vanadium tannate having an intense indigo-blue color.

**A New Method of Tannage.** L. MEUNIER AND A. SEYEWETZ. *Compt. Rend.*, 1908, 146, 987-989.—The authors describe a method of tanning in which hydroquinone (quinol) is employed as the tanning agent. The action takes place only in alkaline solution, and under favorable oxidation conditions. Leather so produced is insoluble, and resists the action of boiling water. Quinone acts equally well, requiring only one per cent. of the weight of the hide. Acid skins tan slowly or not at all, whereas, the action is rapid with alkaline skins. Borax causes negative results. Quinone-tanned leather dyes well with acid, basic, and natural dyestuffs.

**The Use of Sulphurous Acid for Preparing Hides for Tanning.** *La Bourse aux Cuirs, Liége.*—The process is the invention of Eugene Leconte, Sr., who claims that by the use of sulphurous acid, liming and deliming of hides, and the use of expensive acids will be done away with. The acid is an antiseptic and also a powerful and complete plumping agent, at the same time cleansing the hides from blood and other impurities.

Solutions of sulphurous acid are prepared from one to three-tenths of a degree Beaumé, the strength of acid used depending upon the nature and condition of the hides, and the degree of plumpness desired. Without

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previous preparation, the hides are soaked in the acid three or four days, or longer if necessary, after which they are unhaired and fleshed in the usual manner. The hides are then washed free of acid and tanned in the usual way.

**Critical and Experimental Contributions to the Theory of the Tanning Process.** E. STIASNY. *Collegium*, 1908, pp. 117–60.—The writer first discusses the published theories of contemporaries together with some personal experiments bearing on these.

Fahrion declares tanning to be a purely chemical process, leather being a salt in which the hide may act as base or acid. A genuine tanning requires an oxidation of the hide-substance, otherwise a defective leather results, which does not resist water. In vegetable tanned leather, the partially oxidized hide fiber acts as base, the partially oxidized tan as acid. Fahrion assumes in those tan-stuffs which form phlobaphenes, ethylene unions, partially hydrided benzene nuclei. This is not in accordance with the products obtained on fusion with alkali. The absorption of oxygen or iodine need not be explained by ethylene unions as Fahrion himself admits in pointing out the analogy with pyrogallol and other purely aromatic compounds, moreover acetylized tan-stuffs do not absorb iodine. Fahrion assumes that the unsaturated unions act as carriers of oxygen to the hide; ferments may also be agents in this oxidation.

But the tan-stuffs are not easily oxidized except in alkaline solutions which do not occur in the tanning process. Fahrion's view with regard to the hide is that by absorption of oxygen, a product has been formed of increased basic properties. The writer shows experimentally that hide-powder on treatment with hydrogen peroxide is not intensified in acid or basic character. The method consisted in treating 3 grms. of hide-powder with 100 cc. of 1½% peroxide solution for two hours with occasional shaking; 20 cc. of $^1/_5$ normal acid (or alkali) were then added and shaken and an aliquot part of the filtrate titrated back with standard alkali (or acid). Parallel blank experiments were made with pure water substituted for peroxide.

| Three grams hide-powder with | took up after standing ¼ hour | 2 hrs. | 20 hrs. |
|---|---|---|---|
| 100 cc. $H_2O_2$, 20 cc. $^1/_5$ N. HCl ..... | 11.88 | 11.48 | 11.73 cc. $^1/_5$ N. HCl |
| 100 " $H_2O$, 20 " " " ..... | 11.12 | 11.48 | 11.36 " " " |
| 100 " $H_2O_2$, 20 " " NaOH ..... | 3.46 | 1.88 | — — " " NaOH |
| 100 " $H_2O$, 20 " " " ..... | 3.68 | 3.44 | 3.44 " " " |

These experiments show that in considering Fahrion's theory, the reaction of the hide with acids or bases is not modified by a previous oxidation. If the theory of salt formation during tanning is to be retained, the unoxidized hide must be capable of forming salts. But the property of hide-substance of taking up acids or alkalies from aqueous solution is not to be explained by a chemical reaction, but rather as an adsorption process, as shown by the following experiments:

(1). Acids of analogous chemical composition of different strengths were allowed to act in $^1/_{10}$ normal solutions on hide-powder. Assuming a chemical reaction, the stronger the acid, the more should be taken up. Assuming a surface action, the amounts taken up should be the same for anal-

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gous acids. 100 cc. each of the three chlorinated acetic acids ($^1/_{10}$ normal) were allowed to act several hours upon 2 grms. of hide-powder. (A short shaking actually sufficed to produce equilibrium.)

| | Cc. 1/10 N. NaOH used by | | | Millimols acid taken up by 1 grm. hide-powder |
|---|---|---|---|---|
| | 10 cc. original solution | 10 cc. of filtrate | difference | |
| Acetic acid | 10.3 | 9.4 | 0.9 | 0.45 |
| Monochloracetic acid | 10.6 | 9.0 | 1.6 | 0.8 |
| Dichloracetic acid | 10.4 | 8.85 | 1.55 | 0.78 |
| Trichloracetic acid | 10.6 | 9.0 | 1.6 | 0.8 |

This shows that the amounts of the three chlorinated acetic acids taken up were nearly the same. Considering that they are of very different strengths, the affinity constants being in the ratios 1 : 33 : 193, the results speak for an adsorption, all the more since Freundlich (*Habilitations-schrift, Leipzig, 1906*) has found the same agreement of these acids in adsorption experiments with animal-charcoal. The analogy between hide-powder and charcoal also holds good in the lesser adsorption of acetic acid.

(2). A series of experiments were carried out with several aliphatic and aromatic acids. The aromatic acids, although weaker, were taken up in larger amounts, also according with Freundlich's experiments on animal-charcoal.

Millimols acid taken up by 1 grm. hide-powder:

| | |
|---|---|
| Acetic acid | 0.165 |
| Lactic acid | 0.29 |
| Butyric acid | 0.24 |
| Benzoic acid | 0.365 |
| Salicylic acid | 0.43 |
| Picric acid | 0.89 |

While these results in the main agree with those obtained with charcoal, mineral acids behave differently. Charcoal has little absorbent action on these, while hide-powder takes up considerable amounts. Two grms. of hide-powder on treatment with 100 cc. 1/10 normal solutions took up 0.58 millimols hydrochloric acid, 0.76 millimols sulphuric acid, and 0.62 millimols phosphoric acid to 1 grm. hide.

(3). Adsorption experiments were made in aqueous and alcoholic solutions; the results were characteristic of adsorption phenomena, the amounts taken up from the alcoholic solution being less. The hide-powder used was dried to a water content of 0.4 per cent.; the alcoholic acid was prepared by leading dry HCl gas into absolute alcohol.

Millimols acid taken up by 1 grm. hide-powder:

| | |
|---|---|
| From aqueous solution hydrochloric acid | 0.72 |
| From alcoholic solution hydrochloric acid | 0.225 |
| From aqueous solution picric acid | 1.15 |
| From alcoholic solution picric acid | 0.1 |

(4). Experiments with acids of various concentrations showed that relatively more was taken up from dilute than concentrated solutions. Two grms. hide-powder were treated with 100 cc. each of acetic acid solutions.

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| Concentration (approx.) | Per cent. taken up of total used | Millimols of acid taken up by 1 grm. hide |
|---|---|---|
| 2 normal | 2.4 | 2.5 |
| 1 " | 2.4 | 1.25 |
| 0.5 " | 3.9 | 1.0 |
| 0.1 " | 9.4 | 0.5 |
| 0.05 " | 13.2 | 0.35 |
| 0.02 " | 23.6 | 0.25 |
| 0.01 " | 37.7 | 0.2 |

These results plotted graphically give curves similar to those obtained in all adsorption phenomena experiments. Also it was found that in the contact of hide-powder with hydrochloric acid the same end result was obtained independent of the path; for example two grams hide-powder allowed to stand with 20 cc. N. acetic acid and diluted with 80 cc. water, give the same result as when treated directly with 100 cc. of 0.2 N. acid. This also agrees with Freundlich's observations on animal charcoal.

Further supports for the adsorption theory are furnished by the experiments of van Slyke and van Slyke on casein and acids and those of Ostwald on albuminous substances with acids and alkalies; no definite chemical compounds could be obtained.

Fahrion emphasizes the necessity of oxidation of hide fiber in efficient tanning, the resistance of leather to water depending upon this. Although the experiments cited above show that oxidation does not influence the acid or basic character, it might yet be held to affect the absorbing power for tanstuffs. Accordingly experiments were made in this direction. 34.5 grms. of cowhide were left over night in 1% hydrogen peroxide solution, then thoroughly washed and tanned in a gradually strengthened solution of chestnut extract. A parallel experiment was made omitting the peroxide treatment. After two months the two fairly well tanned pieces of leather were rinsed, air dried, and 18 grms. of each used to determine loss by washing which was found to be 15.5% with the previously oxidized leather, and 14.0% with the other. The difference of 1.5% may well be attributed to inequalities and is moreover in the opposite sense as required by Fahrion's theory.

Lumière and Seyewetz found that various phenols made gelatine insoluble in the presence of air and alkali which has been regarded by Nierenstein and by Fahrion as confirming the tanning theory of the latter. The writer considers that this proof fails since tanning is not carried out in alkaline solution.

In mineral tanning, Fahrion considers that in the two bath chrome tannage the hide-substance is oxidized on treatment with bichromate and hydrochloric acid. In the alum-salt tannage, where there can be no such oxidation, he regards the slight water resistance of the leather produced, a direct consequence of the lack of oxidation. The writer made the following experiment showing that previous oxidation does not affect an alum tanned leather.

A sheep-skin was divided in two, one part treated with hydrogen peroxide (2%) for 24 hrs., then soaked in water an equal time and together with

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the other piece which had meanwhile lain in pure water, subjected to an alum-salt tannage.

| | % Ash | Extractible in % of leather | Alumina in % of ash |
|---|---|---|---|
| Glacé leather from oxidized butt | 8.4 | 0.51 | 6.1 |
| Non-oxidized butt | 7.9 | 0.48 | 6.1 |

Finally the production of a leather by the one bath chrome tannage which completely resists extraction with water, speaks against the Fahrion theory (here there is no oxidation).

Another purely chemical theory of tanning is that of Nierenstein who regards leather as a "Schiff's base," the amido groups of the hide having combined with the tannophore groups (—CO—O— or —CO—) of the tanstuffs. The writer doubts if reactive amido groups are really present in hide-substance; that amido-acids are formed on decomposition does not prove amido groups in the original hide. Skraup, Paal, Schiff, Seemann, Richard, Zacharias and others have employed a more rational method, the action of nitrous acid upon albumen, animal fiber, etc. The writer has made some experiment in this direction. 15 grms. hide-powder were well mixed with 50 cc. ½ N.$KNO_2$ solution, strongly cooled, and 60 cc. ½N.HCl added slowly with stirring. The filtered and washed product was dried at 100° and gave 17.8% nitrogen (Kjeldahl), the same as the original hide. Had it been diazotized, a lower or higher nitrogen content would be found, according as the diazo-compounds were unstable or stable. A further argument against the existence of free amido groups may be drawn from the behavior of "diazotized" hide towards acids and bases; if the amido groups are changed into diazo groups, the basic character should be reduced, and should the diazo groups be unstable and converted into phenol groups, the acid character should be increased. Experiment showed that neither takes place.

Absorption in cc. 1/5 N. for 1 grm. hide-powder:

| | Diazotized | Non-diazotized (blank) | Original |
|---|---|---|---|
| Hydrochloric acid | 4.2 | 3.54 | 3.28 |
| Sodium hydrate | 1.33 | 1.45 | 1.93 |

The differences are slight and in opposite sense to that required by theory.

If free amido groups are present in hide and are converted into Schiff's bases by action of formaldehyde, the product should take up less acid than the original hide. Experiments with several acids gave such results. 3 grms. of hide-powder were allowed to stand 24 hrs. with 50 cc. water and 10 cc. formalin, then shaken with 25 cc. of the acid solution in question, and the filtrates titrated with alkali.

| | Cc. 1/5 N. acid taken up | |
|---|---|---|
| | With formaldehyde | Without (blank) |
| Hydrochloric acid | 8.8 | 10.8 |
| Formic acid | 4.67 | 6.71 |
| Acetic acid | 1.76 | 3.6 |
| Picric acid | 6.26 | 7.45 |

The author conscientiously reports these last results, admitting they may be held to support the chemical theory; he suggests however that the for-

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maldehyde treatment may lessen the adsorbing power of the hide. Granted however that reactive, primary amido groups are present in hide, it must be doubted if they would combine with vegetable tan-stuffs with elimination of water to form Schiff's bases. No such compounds are known resulting from primary amines or amino-acids and tan-stuffs. Nierenstein's precipitation of gelatine-salt solutions with tan-stuff solutions is probably not a chemical reaction, but a mutual colloidal separation.

Another objection to the "Schiff's base" theory is that it applies only to the aldehyde and vegetable tannages; for the fat tannage, the intermediate formation of acroleïn is assumed and mineral tannage is not explained at all.

Kopecky's views (This JOURNAL, 1907, p. 380) are next discussed. The writer regards his explanation of chrome tanning as the protection of the fiber by chromium oxide or basic salt, as unsatisfactory and believes the essential feature of mineral tannage to lie in the formation of colloidal basic ingredients by hydrolysis. Kopecky's view that in formaldehyde tanning, the fat of the hide becomes emulsified and protects the fiber from hydrolysis is answered by treating, with formaldehyde, a piece of sheepskin butt from which the fat has previously been extracted with ether; the product has all the properties of formalin tanned leather.

The views of Claflin (This JOURNAL, 1907, p. 457) are rated as purely speculative; what is needed is experimental treatment of the question. Much the same is said of Glücksmann's theories (This JOURNAL, 1907, p. 465); Körner's views (*Jahresber. Freiberg* (1899-1903)) are considered of greater value; he rejects the chemical theory (salt formation) because the two components (hide and tan-stuff) are not electrolytically dissociated; tanning is held to be an adsorption process.

The author next states his own views regarding the tanning process. Every tannage process consists of (1) the adsorption of a colloidal dissolved substance by the hide (2) of secondary changes effected upon the adsorbed substance. Adsorption is defined as what takes place when a substance at its surface occasions the concentration of an adjacent substance, which may be a gas or liquid, the laws being the same for either. For solutions the mathematical expression for equilibrium is $\frac{C_1^n}{C_2} = k$, where $C_1$ is the concentration (amount for unit of volume) of the adsorbed substance, $C_2$ the concentration of the residual solution, and $n$, $k$, constants. This regularity of adsorption phenomena enables one to distinguish whether the action of a solution upon a superficially acting substance like hide is to be considered a chemical process or not. If there is a chemical reaction between tan and hide, then after reaching a certain concentration of solution, a further addition of tan-stuff will result in a chemical union of it with the hide, so that the concentration of the exterior solution remains constant until all the hide particles have combined; then continued addition of tan-stuff will increase the concentration of the exterior solution. The author represents graphically such a process and contrasts the figure with the curve representing the experiments of Wood and Holmes with tannin and chrome hide-powder (*Collegium*, 1906, p. 301); this is regarded as confirming the adsorption theory.

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Colloidal dissolved substances show an individual behavior on adsorption compared with true crystalloidal solutions. Many of the substances employed in tanning belong to this class, although the distinction is not always sharp, and the colloids in question still possess to some extent the characteristics of crystalloids; for example, the vegetable tan-stuffs have a decided power of diffusion through membranes, but their amorphous character, their very slight influence upon the boiling point of water (and consequent high molecular weight) all speak for the colloidal state. Colloids are in general adsorbed to a much greater extent from their solutions than crystalloids; after adsorption they become fixed and insoluble; the adsorption process is not reversible. The distinction can best be observed when the substance concerned exists in both the crystalloid and colloid state, as, for instance, α- and β-silicic acids (Mylius and Groschuff, *Ber. deutsch. chem. Ges.*, 1905, p. 116). α-Silicic acid (crystalloidal) does not precipitate gelatine solution, which is copiously precipitated by a solution of the β-acid (colloidal). This speaks for the colloidal nature of tan-stuffs in their precipitation of gelatine.

Adsorption experiments made by the author showed that 1 grm. hide-powder took up 0.1315 grms. $SiO_2$ from a solution of the β-silicic acid and 0.0170 grms. from a solution of the α-acid, or that the adsorption of the colloidal form was nearly 8 times as great, These results induced a study of the adsorption of tan-stuffs in crystalloidal and colloidal solutions. The molecular weight of tannin determined from aqueous solutions gives values 2643 to 3700; in glacial acetic acid solution, the normal value of 322 is obtained (Paterno), indicating the colloidal and crystalloidal conditions in these solutions respectively.

The author experimented with aqueous and glacial acetic acid solutions of tannin (also quebracho) upon alumina since hide-powder could not be used with the acetic acid; the titrations of residual tannin were made with permanganate. The percentages adsorbed were:

| | Aqueous solution | Glac. acetic acid sol. |
|---|---|---|
| Tannin | 78.5 | 32.0 |
| Quebracho | 99 2 | 53.1 |

*Vegetable Tannage.*—Desirable as it might be to increase our knowledge of the chemical constitution of the complicated vegetable tan-stuffs, the author thinks it would not be of such utility in the explanation of the tanning process as many think. The physical properties are here regarded as of greater influence, diffusion power, relative solubility (or precipitation) on addition of electrolytes, differences of adsorption by substances without chemical action, such as charcoal. The author points out in some detail the harmony between the conditions observed by the practical tanner and the criteria controlling adsorption phenomena in general as laid down by van Bemmelen (*Ztsch. f. anorg. Chem.*, 1903, p. 380).

Increased knowledge of the chemistry of the tan-stuffs will probably find its most important application in the study of the secondary changes effected on the adsorbed bodies. That leather changes with time, yielding less glue on treatment with lime, losing in extractive matter, and other changes all point to chemical alteration.

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The author caused an experiment to be made showing the formation of an insoluble substance by adsorption. Two equal pieces of calf-skin were treated with solution of α-silicic acid 24 hours (ice cooling); one piece was then soaked in pure water 24 hours, dried and ignited; the other was kept moist and warm for 24 hours to convert the α-acid into the colloidal form, and was then washed, dried and ignited. The respective ashes were 1.27 and 2.6 per cent., showing a greater adsorption of the colloidal form.

*Mineral Tannage.*—All salts which can be hydrolytically dissociated, giving a colloidal solution of the basic component, can exert tanning action; a complete hydrolysis however, as with iron salts, is not desirable. For practical tanning, the conditions seem to be that a basic salt should be formed, and while of pronounced colloidal character, should still have a distinct osmotic power, as in the case of the vegetable tan-stuffs; otherwise only the coarse fiber of the hide is affected, there is no penetration and consequently not a useful leather. This double requirement explains the limited number of useful tanning agents.

In many cases two colloids may be prevented from precipitating each other by the protective action of a third colloid, as for example the prevention of gelatine-tan-stuff precipitation by ferric or thorium hydroxide. In the same way an adsorption may be retarded. The author found that an appreciable adsorption of ferric base (using the chloride) by hide-powder was entirely prevented by egg albumen. In a second experiment completely confirming this, the distribution of the chlorine was also determined; the results showed that in the hydrolysis of the dilute ferric chloride solution, the adsorption of the colloidal ferric hydroxide is prevented by the albumen while that of the crystalloidal hydrochloric acid remains the same:

| | With albumen Mgs. | Taken up | Without albumen Mgs. | Taken up |
|---|---|---|---|---|
| Original solu. | 158.5 Fe<br>312.9 Cl | | 158.5 Fe<br>312.9 Cl | |
| After 10 min. | 158.0 Fe<br>214.3 Cl | 0.5 Fe<br>98.6 Cl | 132.0 Fe<br>214.3 Cl | 26.5 Fe<br>98.6 Cl |

Similar experiments with other colloids such as gelatine and gum arabic showed retardation, but not complete prevention of adsorption of iron.

An experiment was made to test the influence of hide peptones on the adsorption of tan-stuffs. Pieces of butt from clear cow hide were allowed to lie in water until putrefaction had well advanced and a portion of the peptone solution thus obtained added to a mallet bark solution and the whole applied to fresh pieces of hide in the shaker; parallel tests were made omitting the peptone solution. It was found that there was no retarding action, both pieces giving the same result. Experiments upon the influence of non-tans gave likewise negative results; the adsorption of quebracho by alumina or sheepskin was not retarded by the addition of oak-wood non-tans. In this and the previous experiment, the residual tan-stuff was determined by formalin precipitation.

Returning to mineral tannage, the author experimented upon retarding the adsorption of chromium chloride by hide-powder; egg albumen, gelatine and hide peptones were found to have no effect. The different behavior

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as compared with iron salts is explained by the more decided colloidal character of the hydrolyzed ferric base. An experiment was made demonstrating the necessity of hydrolytic dissociation in mineral tanning. Hexaurea chromium chloride is analogous in composition to chromium chloride, containing 6 molecules urea in place of 6 molecules of water, but is not hydrolyzed in aqueous solutions which react neutral. It was found to give no appreciable adsorption with hide-powder. An experiment in the same line was made with an alcoholic solution of chromium chloride which was neutral and showed no dissociation (alcoholysis); no adsorption was found with hide-powder.

*Formaldehyde Tannage.*—This differs from ordinary tanning, in the small amount required to produce leather, also the product is remarkably water-proof. Formaldehyde is not adsorbed by charcoal and differs in its action on gelatine from other tanning agents. This tannage differs from others and probably involves a chemical action on the hide albumen.

## PATENTS.

**Hide Working Machine, U. S. Patent No. 890,750.** To J. W. AULSON, Lynn, Mass. An improved hide working machine consisting of an endless carrier provided with a number of blades, adapted to act upon a hide clamped upon a supporting piece. The hide support is provided with toggle mechanism, so that it may be swung to or from a cooperating position with respect to the hide working blades on the endless apron carrier.

**Apparatus for Washing Sheepskins, U. S. Patent No. 891,765.** To C. DUFOUR, Cambridge, Mass. A rotatable tub, having agitators extending inward from its side walls; and a stirrer shaft with lugs, extended into the tub and rotated independently of the tub and in the opposite direction.

**Machine for Treating Hides, Skins and Leather, U. S. Patent No. 891,787.** To F. H. TERL, Peabody, Mass. An improved shaving or buffing machine.

**Process of Recoloring Leather, U. S. Patent No. 891,864.** To E. M. ROBBINS, Buffalo, N. Y. The material to be recolored is first subjected to the action of a bath composed of animal oil, 1 part, vegetable oil, 1 part, ammonia, 1 part and 7 parts of an alcoholic body. This bath is for the purpose of renewing the "life" of the leather, softening, opening the pores, etc. The material is then given a second bath composed of boiled linseed oil, or boiled Chinese wood oil, thinned by the addition of benzine or turpentine, to which is added the desired coloring matter. Gum copal is added if a gloss finish is desired.

**Extractor for Tanning Materials, Fr. Pat. No. 384,566.** S. DEPIGNY AND A. LARMET. The extractor is a vat with one or more transverse partitions above the bottom, two vats, one above the other. The upper vat, with perforated bottom, contains the material to be extracted, and the lower vat contains the extracted liquor. The lower part of the apparatus is provided with a steam coil for maintaining circulation.

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**Wood Chipping Machine, U. S. Pat. No. 892,808.** To OMA CARR, Canton, N. C. An improved chipper for preparing wood for extract or paper manufacture.

**Treatment of Waste Leather, Hoofs, Horns, Etc., of Animals, U. S. Patent No. 892, 840.** To A. G. INRIG, Tottenham, England. The waste material is treated with alkali under heat for a short period, the action is arrested before glue is formed, by cooling the mass and adding dilute acid and again heating and drying the pulp. The product is to be used for shoe heels, fire-proof flooring, partitions, etc., by mixing with sawdust, stannate of soda and hide glue, or with asphaltum, depending on the desired use.

**Use of the Oxidation Products of Phenols, Especially Quinones, for the Tannage of Skins, Fr. Pat. No. 385,057.** A. SEYEWETZ AND L. MEUNIER.—The patent describes the use of phenols and their derivatives (except tannins) for the tanning of skins. The solution must be alkaline and oxidation conditions favorable. Oxidation products of the phenols are also similarly used. The use of these materials in connection with other known tanning substances is covered by the patent.

**Unhairing Agents, Ger. Pat. No. 196,617.** E. KANTOROWICZ.—Mixtures of sulphides with peroxides or per-salts, such as barium, calcium, sodium, magnesium, and zinc peroxides, perborates, percarbonates, etc. were used.

**Leather Substitute, English Patent No. 15,253,** R. WERBER, Vienna-Vegetable or other fibers are impregnated with balata, rubber or gutta. percha by precipitation from the solvent, with acetone, alcohol and methyl alcohol. A complete impregnation of the fibers results and the solvent is recovered.

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## THE ANALYSIS OF LEATHER.[1]

*By A. W. Hoppenstedt.*

The Committee entrusted to investigate this subject was composed of Messrs. R. P. Cushing, C. C. Smoot, III, M. S. McDowell, Dr. J. Gordon Parker, T. Stodola, Robert Hellon, H. G. Patton, J. E. Rhoads and A. W. Hoppenstedt, as Chairman.

Messrs. R. P. Cushing, M. S. McDowell, T. Stodola, Robert Hellon and J. E. Rhoads were unable to serve so that the final

[1] Report of the 1908 Committee.

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Committee consisted of Messrs. H. G. Patton, C. C. Smoot, III, Dr. J. Gordon Parker and the Chairman.

Upon consideration of the subject it seemed to the Chairman that the determination of two points was of importance, namely how close the results of different chemists agree upon the same samples of leather, and whether known amounts of weighting materials in the leather could be found on analysis and accurately determined. In order to establish these points, the Chairman decided to submit to the Committee two samples of leather, the one, a sample of an unsophisticated piece of leather and the other, the same leather but containing known amounts of weighting materials. For this purpose a belting butt was obtained and divided into eight equal squares, according to the following plan:

BELTING BUTT.

| | | | |
|---|---|---|---|
| A | B | A | B |
| B | A | B | A |

The A squares were taken for the sample of pure leather and were ground and thoroughly mixed. This constituted Leather A. The B squares were first weighed and then treated with a definite amount of a solution containing known amounts of glucose and epsom salts and allowed to dry in a cool dark place. After 14 days the squares were reweighed, ground and thoroughly mixed. This constituted Leather B. Accordingly from the above weights and the amounts of glucose and epsom salts put in, and the determination of the moisture of samples A and B, all the necessary data was obtained. The above procedure of treating the leather however was not entirely satisfactory, as will be shown later.

Each member was then supplied with a large sample of Leather A and Leather B and instructed to analyze both samples according to the Provisional Method for Leather Analysis (JOURNAL OF THE AMERICAN LEATHER CHEMISTS ASSOCIATION, 1908, 1, page 7).

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As it seemed advisable to investigate the determination of the glucose volumetrically as well as gravimetrically, the instructions further stated:

"Determine glucose volumetrically as well as gravimetrically according to the following method:

"To 500 cc. of the solution obtained by extraction add 20 cc. of lead sub-acetate, shake well and filter. To 400 cc. of the filtrate add 30 cc. of a saturated solution of sodium sulphate, mix well and filter. To 100 to 400 cc. of the filtrate (according to the amount of glucose present) add 5 cc. of concentrated HCl and boil for two hours, allowing the solution to evaporate to about 50 cc. Make the solution slightly alkaline with NaOH, make up to 100 cc., filter and place the filtrate in a burette. Measure out in a 200 cc. Erlenmeyer flask 10 cc. of standard Fehling solution (measure the 5 cc. of the copper sulphate solution accurately), add about 100 cc. of distilled water, bring to a boil and run in the glucose solution in small amounts, boiling after each addition 1 to 3 minutes according to the amount added. Continue in this way until all the copper has been precipitated. This is determined by filtering a small quantity of the solution into a small test tube, adding a few drops of dilute acetic acid and then one drop of a 10 per cent. solution of potassium ferrocyanide, allowing the same to run down the side of the tube. Any copper still present will be indicated by a brown-red precipitate or a brownish coloration according to the amount still present. The end point of the titration is reached when a reaction is no longer obtained, care being taken that this takes place on the addition of not more than 0.5 cc. of the glucose solution. It is not necessary to commence testing for copper until the blue color of the solution has disappeared. The 10 cc. of Fehling solution is equal to 0.05 gms. of glucose, thus from the amount of the glucose solution used to precipitate all the copper, the percentage of glucose can readily be figured. In case a leather contains only a trace of glucose, the strength of the solution from the leather will not be sufficient to precipitate all the copper."

The results on the two samples of leather as reported to the Chairman by the members of the Committee, on the leather as received by them, were as follows:

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LEATHER A.

| | Patton. | Smoot. | Parker. | Hoppenstedt. |
|---|---|---|---|---|
| Moisture | 10.51 | 9.75 | 11.30 | 11.31 |
| Oil | 4.87 | 4.57 | 4.98 | 4.60 |
| Ash | 0.34 | 0.31 | 0.40 | 0.31 |
| Hide | — | 39.17 | 40.00 | 39.16 |
| Combined tannin | — | 31.80 | 25.72 | 28.37 |
| Uncombined tannin | — | 8.68 | 12.00 | 9.34 |
| Uncombined non-tannins | — | 5.72 | 5.60 | 6.91 |
| Nitrogen | — | 6.97 | 7.10 | 6.97 |
| Water solubles | — | 14.40 | 17.60 | 16.25 |
| Glucose, gravimetric | — | 0.42 | 0.58 | 0.45 |
| Glucose, volumetric | — | — | — | — |
| Epsom salts | — | 0.14 | — | 0.11 |

LEATHER B.

| | Patton. | Smoot. | Parker. | Hoppenstedt. |
|---|---|---|---|---|
| Moisture | 8.63 | 8.78 | 10.40 | 9.41 |
| Oil | 4.31 | 4.03 | 4.40 | 4.10 |
| Ash | 1.02 | 0.99 | 1.00 | 0.97 |
| Hide | — | 35.53 | 36.00 | 35.39 |
| Combined tannin | — | 29.43 | 22.10 | 27.05 |
| Uncombined tannin | — | 7.89 | 12.10 | 7.94 |
| Uncombined non-tannins | — | 14.40 | 14.00 | 16.11 |
| Nitrogen | — | 6.32 | 6.41 | 6.30 |
| Water solubles | — | 22.29 | 26.10 | 24.05 |
| Glucose, gravimetric | — | 7.69 | 7.20 | 7.13 |
| Glucose, volumetric | — | 7.43 | 7.40 | 7.27 |
| Epsom salts | 3.14 | 3.05 | 2.93 | 3.17 |

These results calculated on the dry leather show:

LEATHER A.

| | Patton. | Smoot. | Parker. | Hoppenstedt. |
|---|---|---|---|---|
| Oil | 5.44 | 5.06 | 5.61 | 5.19 |
| Ash | 0.38 | 0.34 | 0.45 | 0.35 |
| Hide | — | 43.40 | 45.10 | 44.15 |
| Combined tannin | — | 35.24 | 29.00 | 31.99 |
| Uncombined tannin | — | 9.62 | 13.53 | 10.53 |
| Uncombined non-tannins | — | 6.34 | 6.31 | 7.79 |
| Nitrogen | — | 7.72 | 8.00 | 7.86 |
| Water solubles | — | 15.96 | 19.84 | 18.32 |
| Glucose, gravimetric | — | 0.47 | 0.65 | 0.51 |
| Glucose, volumetric | — | — | — | — |
| Epsom salts | — | 0.16 | — | 0.12 |

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LEATHER B.

| | Patton. | Smoot. | Parker. | Hoppen-stedt. |
|---|---|---|---|---|
| Oil | 4.72 | 4.42 | 4.91 | 4.53 |
| Ash | 1.12 | 1.09 | 1.12 | 1.07 |
| Hide | — | 38.95 | 40.18 | 39.07 |
| Combined tannin | — | 32.26 | 24.66 | 29.85 |
| Uncombined tannin | — | 8.65 | 13.50 | 8.77 |
| Uncombined non-tannins | — | 15.79 | 15.63 | 17.78 |
| Nitrogen | — | 6.93 | 7.15 | 6.95 |
| Water solubles | — | 24.44 | 29.13 | 26.55 |
| Glucose, gravimetric | — | 8.43 | 8.04 | 7.87 |
| Glucose, volumetric | — | 8.15 | 8.26 | 8.03 |
| Epsom salts | 3.44 | 3.34 | 3.27 | 3.50 |

On the whole these results agree fairly well. A discussion of each determination follows:

*Moisture.*

This determination seems satisfactory. Dr. Parker says that by drying in an air oven at 100°C. slightly higher results are obtained. Experiments made by the Chairman, drying for 2 hours at 110° C. in an air oven compared with the Provisional Method, gave no difference in results.

*Oil.*

No remarks. Seems satisfactory.

*Ash.*

No remarks. Seems satisfactory.

*Nitrogen or Hide.*

This determination also seems satisfactory. Dr. Parker states that the use of $KMnO_4$ instead of $K_2SO_4$ hastens the destruction considerably, with no difference in results. Boil first for ¼ hour, let cool, add ½ gram of $KMnO_4$, and heat up again. Finished in 1 hour instead of 4-5. Experiments made by the Chairman with the Provisional Method by adding 1 per cent. NaCl, 4 per cent. NaCl, 2 per cent. $BaCl_2$ and 4 per cent. $BaCl_2$ showed that the addition of these chlorides had no effect on the results.

*Water Solubles, Uncombined Tannin, Uncombined Non-Tannins.*

The results on these determinations seem to vary to some extent and the difference seems mostly due to tannin. Mr. Smoot

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gives an outline of a method for the determination of the water solubles which was worked out in the Bureau of Chemistry, U. S. Department of Agriculture, and is as follows:

Treat ten grams of leather in some form of extractor that will allow the continuous percolation of liquid for seven hours, at the same time keeping the volume of percolated liquid within one liter, the extraction to be made at 50° C. The first 200 cc. may be collected in an outside flask while the solution in the receiving flask is changed and added to the first portion in a liter flask as concentration demands. The extraction may be then continued in a similar manner for seven hours additional, making the total volume two liters if desired.

Results by this method:

| | Leather A. | Leather B. |
|---|---|---|
| Total solids, 1st liter | 22.84 | 29.96 |
| Total solids, 2nd liter | 2.52 | 2.76 |
| Total extract | 25.36 | 32.72 |
| Uncombined tannin | 18.oc | 15.58 |
| Uncombined non-tannins | 7.36 | 17.14 |

Mr. Smoot says that the results obtained by this method are considerably higher than those obtained by the Provisional Method and that there is no evidence of a breaking up of the leather, results of a fairly concordant value being obtained. In the opinion of the Chairman however the results point very strongly to a breaking up of the leather as the increase is practically all due to tannin. This is further substantiated by experiments made with the Provisional Method by the Chairman with slight variations in the manipulation, when 24.05, 25.92 and 26.75 per cent. of water solubles were obtained on Leather B. The increase here also being almost entirely due to tannin. The Chairman therefore feels that the determination of the water solubles should be further investigated.

*Combined Tannin.*

This value also varies to some extent being principally influenced by the difference in the water solubles. Besides this there seems to be no real understanding for the calculation of the same. In general, on leathers which have a high ash, due to weighting materials, the ash is not included in the calculation. It seems to the Chairman that the proper way of allowing for the ash, is to determine the same in the water solubles and to deduct this

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amount from the total ash, putting the difference in the calculation. He therefore desires to submit this procedure for consideration.

*Glucose.*

The results on this determination agree pretty well. Mr. Smoot says: "The results on the determination of glucose by the Provisional Method and also by the proposed volumetric method are widely divergent, which is undoubtedly due to the too great concentration of the acid solution. The concentrations employed will destroy small quantities of sugar, as was noted by Mr. Veitch in the April number of the JOUR. A. L. C. A. The results obtained on the same solution by our laboratory method were more uniform and higher." The method referred to is as follows:

Take 500 cc. of the first liter of solution obtained by extraction as per L. & P. Lab. Method, treat with 25 cc. of lead sub-acetate, shake well and allow to stand for several hours, filter and treat with $K_2SO_4$ or anhydrous $Na_2CO_3$, filter and to 420 cc. of the filtrate add 5 cc. of HCl and boil down to 175-190 cc. and then for two hours with reflux condenser, cool, neutralize, filter if necessary, and make up to 200 cc. Treat aliquot portion with Fehling solution in the usual manner, being careful to keep total volume 145 cc. as specified.

Results by this method:

| | Dry leather | |
|---|---|---|
| | A. | B. |
| Glucose, Provisional method of extraction ..... | 0.63 | 8.66 |
| Glucose, L. & P. Lab. method of extraction ..... | 0.83 | 9.58 |

The Chairman considers these results extremely high as will be shown later in the calculations of the amounts added to the leather.

Dr. Parker says: "Journal III. April, page 108, note by Mr. F. P. Veitch, true. Boiling in open vessel for 2 hours gives lower results. The inverting of the glucoside matters has to be done for 2 hours in boiling water-bath with inverted condenser, using 10 per cent. (of the volume of the liquor) of strong hydrochloric acid. In the case of Leather B. where glucoses are present abundantly:

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200 cc. of extract of water soluble material (=3 gr. Leather)
20 cc. Basic lead acetate.
Let stand for ¼ hour, stir well.
Filter; take 110 cc. filtrate.
110 cc. filtrate = 100 cc. original solution.
20 cc. sodium sulphate.

---

130 cc.

Filter off lead sulphate

100 cc. of this filtrate inverted with 10 cc. strong hydrochloric acid, first heat up to boiling on free flame, then in boiling water-bath for 2 hours.

Neutralize, filter, and estimate in these 100 cc. glucose with 60 cc. of the Fehling, and proceed as in Provisional Method."

Results by this method:

| | Dry leather A. | Dry leather B. |
|---|---|---|
| Glucose | 0.65 | 7.98 |

Dr. Parker further says: "The volumetric method is not accurate enough, though it is of great use in ascertaining roughly the amount of glucoses present. With Leather A. it was of no use, only containing a trace of glucose, the liquor was not strong enough. The precipitation of the excess of lead acetate can be done either by sodium carbonate or sodium sulphate. No material differences were found. If the $Cu_2O$ is oxidized to CuO and the factor as given by Allen "Comm. Analysis" Vol. I., be used, 1 gram CuO=0.4535 dry glucose, the results will be found higher than the ones got by using the tables of Koch and Ruhsam."

Dr. Parker concludes that the points which require settling are: a definite table for the estimation of glucose, and a definite method for inverting the glucoses.

The Chairman has found from a number of years of experience with the volumetric method that the results are very satisfactory, but he does not recommend the method, as very small quantities of glucose, as in Leather A., cannot, without difficulty, be determined by it. He agrees with Mr. Smoot and Dr. Parker regarding the inversion of the glucose and recommends that work be done on this subject and a better method established. In regard to the definite table for the estimation of the glucose, the

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Chairman is of the opinion that the one by Koch and Ruhsam, as given in the Provisional Method, is fully satisfactory. The results by the volumetric method further indicate this, especially those which follow later, on the glucose solution put in the leather.

We now come to the most interesting part of the work, the comparison of the results of Leather A., calculated on the basis of Leather B., with those obtained on Leather B., and the comparison of the amounts put in the leather with those actually found.

The treatment of Leather B., which was outlined at the beginning, gave the following values:

| Weight of dry leather | | Total increase in weight |
|---|---|---|
| Before treatment | After treatment | |
| 1603.87 grams | 1761.16 grams | 157.29 grams |

This increase is equal to 8.93 per cent. of the leather after treatment and consequently represents the total amount of dry substances added to and contained in Leather B.

The leather was treated with 653 grams of a solution containing:

| | |
|---|---|
| Glucose, according to gravimetric method | 24.15% |
| Glucose, according to volumetric method | 23.87% |
| Epsom salts | 8.87% |

so that there was added to Leather B:

| | |
|---|---|
| Glucose, according to gravimetric method | 8.95% |
| Glucose, according to volumetric method | 8.85% |
| Epsom salts | 3.29% |

This makes the total amount of weighting materials added, as follows:

| | Gravimetric | Volumetric |
|---|---|---|
| Glucose | 8.95% | 8.85% |
| Epsom salts | 3.29% | 3.29% |
| Total | 12.24% | 12.14% |
| Total amount added according to actual weight | 8.93% | 8.93% |
| Apparent loss | 3.31% | 3.21% |

These results do not agree very well but the apparent reason for the same will be seen later. The following table shows the results on Leather A. calculated to the basis of Leather B. and

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compared with the results obtained on Leather B., all being calculated on the dry leather.

TABLE A.

| | Patton | | Smoot | | Parker | | Hoppenstedt | |
|---|---|---|---|---|---|---|---|---|
| | A basis B | B | A basis B | B | A basis B | B | A basis B | B |
| Oil | 4.95 | 4.72 | 4.61 | 4.42 | 5.11 | 4.91 | 4.73 | 4.53 |
| Hide | — | — | 39.52 | 38.95 | 41.07 | 40.18 | 40.21 | 39.07 |
| Combined tannin | — | — | 32.09 | 32.26 | 26.41 | 24.66 | 29.13 | 29.85 |
| Uncombined tannin | — | — | 8.76 | 8.65 | 12.32 | 13.50 | 9.59 | 8.77 |
| Uncombined non-tannins | — | — | 5.77 | 15.79 | 5.75 | 15.63 | 7.09 | 17.78 |
| Nitrogen | — | — | 7.03 | 6.93 | 7.29 | 7.15 | 7.16 | 6.95 |
| Glucose | — | — | 0.43 | 8.43 | 0.59 | 8.04 | 0.46 | 7.87 |
| Epsom salts | — | 3.44 | 0.15 | 3.34 | — | 3.27 | 0.11 | 3.50 |

The two following tables indicate the amounts of weighting materials found added to Leather B.

TABLE B.

| | Smoot | | Parker | | Hoppenstedt | |
|---|---|---|---|---|---|---|
| | Grav. | Vol. | Grav. | Vol. | Grav. | Vol. |
| Glucose found in Leather B | 8.43 | 8.15 | 8.04 | 8.26 | 7.87 | 8.03 |
| Glucose originally in Leather B | 0.43 | 0.43 | 0.59 | 0.59 | 0.46 | 0.46 |
| Glucose found added to Leather B | 8.00 | 7.72 | 7.45 | 7.67 | 7.41 | 7.57 |

TABLE C.

| | Patton | Smoot | Parker | Hoppenstedt |
|---|---|---|---|---|
| Epsom salts found in Leather B | 3.44 | 3.34 | 3.27 | 3.50 |
| Epsom salts originally in Leather B | 0.13 | 0.15 | 0.13 | 0.11 |
| Epsom salts found added to Leather B | 3.31 | 3.19 | 3.14 | 3.39 |

The average of these results compared with the amounts actually put in, show the following:

TABLE D.

| | Gravimetric | Volumetric |
|---|---|---|
| Glucose added to Leather B | 8.95 | 8.85 |
| Average glucose found added to Leather B | 7.62 | 7.65 |
| Loss | 1.33 | 1.20 |

TABLE E.

| | |
|---|---|
| Epsom salts added to Leather | 3.29 |
| Average Epsom salts found added to Leather B | 3.26 |
| Loss | 0.03 |

The total weighting materials found added to Leather B. are then as follows:

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TABLE F.

| | Gravimetric | Volumetric |
|---|---|---|
| Average glucose found added to Leather B..... | 7.62 | 7.65 |
| Average Epsom salts found added to Leather B.. | 3.26 | 3.26 |
| Total weighting materials found added to Leather B | 10.88 | 10.91 |

These compared with the total amounts added to Leather B., show the following:

TABLE G.

| | Gravimetric | Volumetric |
|---|---|---|
| Total weighting materials added to Leather B ... | 12.24 | 12.14 |
| Total weighting materials found added to Leather B | 10.88 | 10.91 |
| Loss ..... | 1.36 | 1.23 |

The next table shows the calculated total amount added to Leather B. according to the difference in the results obtained on Leather A. and Leather B., and compared with the amount indicated by the actual weight.

TABLE H.

| | Patton | Smoot | Parker | Hoppenstedt |
|---|---|---|---|---|
| According to the oil..... | 13.24 | 12.65 | 12.48 | 12.72 |
| According to the nitrogen .... | .... | 10.23 | 10.62 | 11.58 |
| According to the non-tannins. | .... | 10.02 | 9.88 | 10.69 |
| According to the actual weight | 8.93 | 8.93 | 8.93 | 8.93 |

The final tables show the difference in the Oil and the Nitrogen obtained on Leather A calculated to the basis of Leather B., and the results obtained on Leather B.

TABLE I.

| | Patton | Smoot | Parker | Hoppenstedt |
|---|---|---|---|---|
| Oil, A. calculated to basis of B. | 4.95 | 4.61 | 5.11 | 4.73 |
| Oil, B..... | 4.72 | 4.42 | 4.91 | 4.53 |
| Loss..... | 0.23 | 0.19 | 0.20 | 0.20 |

TABLE J.

| | Smoot | Parker | Hoppenstedt |
|---|---|---|---|
| Nitrogen, A. calculated to basis of B.... | 7.03 | 7.29 | 7.16 |
| Nitrogen, B..... | 6.93 | 7.15 | 6.95 |
| Loss ..... | 0.10 | 0.14 | 0.21 |

All these results seem rather puzzling at first sight but on careful consideration, the truth seems apparent. Evidently fermentation set in after the leather had been treated and during the course of drying, causing a loss in the glucose and a partial breaking up of the leather. This is indicated by all the results

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shown in the tables from A. to J. Some years ago the Chairman carried out experiments similar to these but employing a more concentrated solution of glucose for treatment of the leather and also allowing the leather to dry for only two days after which it was analyzed. The results obtained on analysis were excellent and showed the same amounts that had actually been put in the leather. The Chairman therefore feels that he can account for the action which apparently took place in Leather B.

Tables A, B and C commence to indicate the discrepancies in the results. Table D shows the loss in the glucose, while Table E shows that the correct amount of Epsom Salts was found. Tables B and D also show how very favorably the results on the glucose by the volumetric method compare with those by the gravimetric method. Tables F and G indicate the loss in the total amount of weighting materials added, the same being entirely due to the glucose. Table H does not show the conditions very plainly. The high amounts shown by the oil point to a breaking up of the same, this being further seen in Table I by the loss in the oil. The amounts shown by the nitrogen indicate a breaking up of the hide, this is distinctly shown in Tables A and J. The figures given by the non-tannins were obtained by deducting the amounts obtained on Leather A. calculated on the basis of Leather B., from the amounts obtained on Leather B. They should agree with the total amounts found added to Leather B. and do so to a certain extent. The amount shown by the actual weight is naturally greatly influenced by the changes which took place in the leather and so is no real criterion.

It is thus seen that a loss has taken place in the oil, hide and glucose and apparently there has also been a loss in the tannin, the latter being indicated by the results of Mr. Smoot and the Chairman in Table A. The results all tend to show that the maximum amount of weighting materials present in Leather B. were found on analysis. The finding of the correct amount of Epsom salts strengthens this deduction considerably and the great difference between the amounts of weighting materials put in and the actual increase in weight of the leather after treatment, leaves little doubt that considerable changes had taken place, and that the full amounts originally put in could no longer be present.

The general conclusions to be drawn from the work of the

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Committee would be, that with the present method the results of different chemists on the same sample of leather, agree fairly well, the only weak points indicated being, the determination of the water solubles and consequently the combined tannin, and the inversion of the glucose. Thus a summary of the recommendations made, reads:

1. Further investigation of the determination of the water solubles.
2. Uniform method for calculating the combined tannin.
3. Investigation and improved method for inverting the glucose.

## STANDARD METHODS FOR THE ANALYSIS OF MATERIALS USED IN MAKING CHROME LEATHER.[1]

*By W. H. Walker.*

After some preliminary correspondence undertaken for organization of the Committee and the definition of its scope, the following letter was sent by the Chairman to each of the members:

I herewith enclose tentative methods for the analysis of commercial bichromates of sodium and potassium and hyposulphite of soda. These procedures are based upon methods forwarded by various members of the Committee, and are in some cases nearly identical with the directions as sent to me. As you are aware, one of the ultimate objects of the Committee is to formulate standards which will be acceptable to both the buyer and seller of the materials used in chrome tanning. The enclosed procedures include those for the determination of "total chrome" and of neutral chromate or free chromic acid in bichromates, and the determination of reducing power of hyposulphite of soda.

I desire to ask your opinion as to whether the above determinations are sufficient as a basis for the sale of these materials, or should additional tests for the amount of sulphate and chloride in bichromates, for example, and the neutral sulphite and sulphate in hyposulphite of soda, be included in our standard methods.

I am sending you under separate cover, samples of commercial bichromate of potash and hyposulphite of the soda, and will ask you to analyze these at your earliest convenience, using each of the enclosed methods, and to send me your results together with

[1] Report of the 1908 Committee.

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any suggestions or criticisms which you may have to offer. In deciding upon a standard method for the analysis of any material, we must consider the accuracy, rapidity and convenience of the procedure, and I would ask you to give me your opinion on these points, especially in connection with methods (1) and (2) for the determination of total chromium in bichromates, and as to the best method for determining free chromic acid.

## TENTATIVE METHODS FOR ANALYSIS OF BICHROMATES.

### *Determination of Total Chromium.*

#### *Procedure No. 1.*

*Solutions Required:*

(1) Ferrous Ammonium Sulphate. Dissolve 40 grams $FeSO_4.(NH_4)_2SO_4.6H_2O$ (hereinafter referred to as "F. A. S." in one liter of water containing 15 cc. concentrated $H_2SO_4$ (sp. gr. 1.84). Standardize against C. P. $K_2Cr_2O_7$ using the same procedure as in analysis of sample and described below.

(2) Bichromate of Potash. Heat to fusion a sufficient quantity of pure, recrystallized $K_2Cr_2O_7$, and after cooling in a desiccator, dissolve 0.5 gram in about 50 cc. water and dilute to one liter.

(3) Potassium Ferricyanide. Dissolve 0.5 gram C. P. $K_3Fe(CN)_6$ in 100 cc. water.

(4) Sulphuric Acid. One part $H_2SO_4$ (sp. gr. 1.84) to three parts water.

*Analysis of Sample.*

Dissolve 5 grams of the sample of either $K_2Cr_2O_7$ or $Na_2Cr_2O_7.2H_2O$ in one liter of water. Measure off with a pipette 50 cc. of this solution (equivalent to 0.25 gram of sample) in a porcelain dish. Dilute to about 200 cc. and add 10 cc. sulphuric acid. From a burette run in about 45 cc. "F. A. S." solution, with constant stirring. Test at this point by removing a very small drop of the solution and mixing with a drop of the potassium ferrocyanide indicator on a porcelain tile. If no blue color appears, continue to add the "F. A. S." in 0.5 cc. portions until a slight excess of the latter is present, the bichromate of potash solution (2) is then run in, drop by drop, from another burette until the point is reached where no blue color appears after the lapse of 30 seconds from the time of mixing solution and indi-

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cator on the tile. To accurately determine the end-point, as soon as 30 seconds have elapsed remove another drop of the solution and test, placing it beside the last previous mixture. If the latter shows a blue color in comparison with the fresh mixture, the end point has not been reached; if no difference can be noted, the reaction is complete.

NOTE 1. The reaction which takes place is

$$6Fe(SO_4)+K_2Cr_2O_7+7H_2SO_4=3Fe(SO_4)_3+Cr_2(SO_4)_3+K_2SO_47H_2O.$$

NOTE 2. As bichromate of soda is deliquescent it should always be weighed from a stoppered tube.

NOTE 3. The ferrous ammonium sulphate solution changes in value rapidly and should be standardized frequently. It should be kept as nearly as possible to such a strength that 100 cc.-0.5 gram $K_2Cr_2O_7$. If this concentration be maintained, a tedious calculation is eliminated as the standard bichromate of potash solution is made exactly one-tenth this strength. For example, if 1.5 cc. of the latter solution be used in the final titration, 0.15 cc. may be at once subtracted from the amount of ferrous ammonium sulphate solution used. If, however, the ferrous ammonium sulphate solution differs from the prescribed concentration, an appreciable error is introduced in making this correction.

NOTE 4. The potassium ferricyanide solution is not stable and should be freshly prepared for use. It must of course contain no ferrocyanide for which it should be tested by adding to a portion a drop or two of $FeCl_3$. If the latter is present it may be oxidized by the addition of a little bromine, and the ferricyanide re-crystallized.

NOTE 5. In heating the bichromate, the fusion temperature must not be exceeded, or the salt will lose oxygen.

NOTE 6. The time indicator for the indicator tests must be carefully noted. The completion of the reaction between the ferrous ammonium sulphate and the potassium ferricyanide takes an appreciable time. Thirty seconds is a convenient interval.

NOTE 7. The accuracy of the titration may be much impaired by the removal of unnecessarily large quantities of solution for testing.

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*Procedure No. 2.*

*Solutions Required:*

(1) Tenth-Normal Sodium Thiosulphate. Standardize against pure bichromate of potash using the procedure described below.

(2) Potassium Iodide. Dissolve 150 grams of the C. P. salt in one liter of water.

(3) Hydrochloric acid (sp. gr. 1.2).

(4) Starch solution. If the soluble starch is at hand, dissolve 0.5 gram in 25 cc. boiling water. 1 to 2 cc. of the cold solution is sufficient for a titration. If soluble starch is not available potato starch may be used. Mix one gram with 5 cc. cold water to a smooth paste. Pour 150 cc. boiling water over it, warm for a moment and set aside to settle. Decant the supernatant liquid through a filter and use the clear filtrate. Five cc. are needed for a titration.

*Analysis of Sample.*

Dissolve 5 grams of the sample in one liter of water as in Procedure No. 1. Measure off with a pipette 25 cc. of this solution (equivalent to 0.125 gram of sample) in a glass stoppered flask or bottle. Add 5 cc. hydrochloric acid and 20 cc. of the potassium iodide solution and let stand with frequent shaking for five minutes. Run in the sodium thiosulphate from a burette until the yellow color of the liberated iodine has almost disappeared, and the required amount of starch solution and continue the titration until the blue color of the iodo-starch changes to the greenish tint of chromium chloride.

NOTE 1. The reactions which take place are:

$$K_2Cr_2O_7+14HCl=2CrCl_3+2KCl+3Cl_2+7H_2O;$$
$$3Cl_2+6KI=6KCl+3I_2;$$
$$3I_2+6Na_2S_2O_3=3Na_2S_4O_6+6NaI.$$

NOTE 2. The sodium thiosulphate solution is not stable and should be standardized frequently. It must be protected from light and heat as both promote decomposition.

NOTE 3. The potassium iodide must be free from iodate, which may be tested for by acidifying with hydrochloric acid,

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which liberates iodine if iodate is present, coloring the solution brown and giving the iodo-starch reaction.

NOTE 4. The hydrochloric acid must be free from chlorine, which may also be detected by a blank test.

NOTE 5. Complete settling of the starch solution is necessary for if the solid particles of starch are not removed, they become so colored by the iodine that they are not easily decolorized by the sodium thiosulphate, and impair the delicacy of the reaction.

NOTE 6. Care must be taken that iodine is not lost by volatilization; the flasks should be kept closed until ready for titration.

*Determination of Neutral Chromate or Free Chromic Acid.*

*Procedure No. 1.*

*Solutions Required:*

(1) Tenth-Normal Potassium Hydroxide.

(2) Phenolphthalein. Dissolve one gram in 100 cc. 95 per cent. alcohol.

*Analysis of Sample.*

Measure off with a pipette 100 cc. of the sample solution (equivalent to ½ gram of the salt) already prepared for the determination of the total chromium. Add five drops phenolphthalein and titrate with the potassium hydroxide to pink coloration. If on calculation, the results agree with those of the determination of the total chromium, the sample contains neither neutral chromate nor free chromic acid. An excess is calculated to free chromic acid and a shortage to neutral chromate.

NOTE 1. The reaction which takes place is

$$K_2Cr_2O_7+2KOH=2K_2CrO_4+H_2O.$$

NOTE 2. During the titration of the acid in bi-chromates the indicator is oxidized so rapidly that several additions of phenolphthalein are sometimes necessary before the end point is finally reached, but quite good results can be obtained, especially if a comparative test is made with some C. P. salt.

*Procedure No. 2.*

This is identical with No. 1 except that the end-point is de-

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termined by means of a stronger solution of phenolphthalein (5 grams in 100 cc. 95 per cent. alcohol) the indicator being placed upon a porcelain tile and drops of the solution mixed with it.

*Procedure No. 3.*

Repeat Procedure No. 1, but do not add phenolphthalein until 95 per cent. of the chromic acid, as found by the first titration, has been neutralized.

## TENTATIVE METHOD FOR ANALYSIS OF HYPOSULPHITE OF SODA.

*Determination of Total Reducing Power.*

*Solutions Required:*

(1) Tenth-Normal Bichromate of Potash. Heat to fusion a sufficient quantity of pure, re-crystallized $K_2Cr_2O_7$, and after cooling in a desiccator, dissolve 4.9083 grams in one liter of water.

(2) Potassium Iodide. Dissolve 150 grams of the C. P. salt in one liter of water.

(3) Hydrochloric acid (sp. gr. 1.2).

(4) Starch Solution. See Procedure No. 2 for the determination of total chromium.

*Analysis of Sample.*

Dissolve 25 grams of the sample in one liter of water. Measure off with a pipette 25 cc. of the tenth-normal bichromate of potash into a glass-stoppered bottle or flask. Add 5 cc. hydrochloric acid and 15 cc. of the potassium iodide solution. Let stand with frequent shaking for five minutes. Titrate the liberated iodine with the hyposulphite sample solution, exactly as given in Procedure No. 2 for the determination of total chromium.

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It is to be regretted that because of pressure of routine duties, or other causes, the responses from the members have been so few and meagre; those received are submitted without comment, and with the hope that the methods proposed will stimulate criticism that will beget further work on this subject.

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CHROME COMMITTEE COLLABORATIVE WORK.

| Member | $K_2Cr_2O_7$ Proc. 1 % | $K_2Cr_2O_7$ Proc. 2 % | Neutral chromate Proc. 1 % | Neutral chromate Proc. 2 % | Neutral chromate Proc. 3 % | $Na_2S_2O_3.5H_2O$ % |
|---|---|---|---|---|---|---|
| Alden | 99.78 | 99.38 | 1.76 | | 1.76 | 97.59 |
| Bower | 99.70 | 99.62 | None | None | None | 98.62[1] |
| White | 99.57 | 99.78 | 2.25 | None | 1.52 | 97.28[2] |
| Walker, Asst. No. 1 | 99.82 | 99.80 | 0.23 | | 0.23 | 97.86 |
| Asst. No. 2 | 99.65 | 99.70 | None | | None | 97.68 |

[1] Repeated the determination and obtained same result.

[2] Repeated determination and obtained 98.78 per cent., but is not confident of the accuracy of either result.

## PRESERVATIVE EFFECT OF BORO-PHENOL UPON CHROMED HIDE-POWDER.[1]

*By Dr. J. Gordon Parker and Alex T. Hough.*

There is a general tendency nowadays for the works chemist to have more and more to do with the works management and less and less with actual laboratory practice, the methods for which must consequently be as accurate and rapid as possible, so that they may be carried out with a minimum loss of time.

It has not been claimed, nor ever will be, that the present official method of the I. A. L. T. C. for estimating tannins is all that can be desired in time-saving methods, and any modification which can be forwarded with a view to reducing the time and labor required in this more or less laborious method, without violating the rules, is a thing much to be desired, at least from the point of view of those who are continually being called upon to analyze tanning agents containing tannic acid.

Now that the eternal question of a suitable hide-powder and its standardization is nearing complete settlement, the authors thought it advisable to apply their efforts to other parts of the process, with a view to lessening the labor required of the tannin analyst, and subsequently turned their attention to that *bête noir* of the whole process, viz., the washing of the chromed hide-powder. This may later, under the new scheme of work formulated by Professor Procter for the Commission, be entirely obviated, but for the present we may safely assume its continuance for some months to come.

[1] From the *Collegium*.

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The greater part of the objections against the preparation of the hide-powder are directed more to the fact that it must be prepared fresh every day, than towards any other point, and many chemists would be quite mollified if a week's supply could be prepared at once, but under the present conditions the hide-powder would be quite unfit for use after the third day of standing.

In view of the above facts the authors commenced to look about for a suitable preservative which would not, at the same time, affect the condition of the hide-powder; and ultimately found that boro-phenol could not be superseded for the purpose, giving excellent results. The preservative is made and used as follows:

A stock solution is made by dissolving 10 grams (absolute) phenol and 20 grams boracic acid in 1 liter of cold distilled water. The hide-powder, after washing free from solubles, chlorides, etc., and squeezing, is placed in a sterile air-tight bottle; an ordinary 2 to 4 lb. wide-necked bottle will serve the purpose, after washing out with a little boro-phenol and distilled water. The stock boro-phenol is then diluted to one-tenth of its original strength with distilled water, so that the strength of the solution is now 1 part per 1,000 phenol and 2 parts per 1,000 boracic acid, sufficient of this solution being prepared as will conveniently cover the powder; it is then poured on the powder, and the bottle is closed with a rubber stopper.

When required for use the whole of the contents of the bottle is thrown on a cloth, allowed to drain, washed once with distilled water, squeezed and weighed; an aliquot part, to equal 6.5 grams dry hide, is then weighed out for each shake, and the remainder is returned to the bottle with a fresh supply of boro-phenol.

The above method requires that the whole of the powder shall be squeezed and washed, where only part of it is required, and there is this argument in favor of it. The powder which remains is kept all the fresher by being washed once daily and having each day a fresh charge of boro-phenol. But the following alternative method works equally well, and prevents washing a large bulk of powder which is not required.

Suppose that the laboratory is analyzing fairly regularly three samples of tanning extracts or liquors in duplicate per day; this

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means six shakes, or thirty-six shakes per week of six working days. Enough powder for thirty-six shakes is standardized, chromed and washed as usual and then divided up into six separate lots, each enough for six shakes, or one day's work; each lot is then placed in a separate bottle with a sufficiency of boro-phenol and the contents of one bottle used every day, squeezing and washing once as before described, then weighing out the quantity "Q" equalling 6.5 grams of dry hide, and making up to (26.5 —"Q") grams with distilled water, etc., etc., as prescribed for the official method.

The accuracy of the method and the preservative action of boro-phenol is sufficiently well shown in the tables, and the authors trust that the method will prove its value in those laboratories where tanning analyses are continually being made.

It was at first suggested by one of us that the boracic acid might upset the basicity of the powder, but it does not seem to exert any influence in that direction even after prolonged action. The agreement of the figures in the tables also bear this out.

Each of the results below are the mean of at least two analyses, in several cases the mean of 5 separate tests by two different analysts.

| Extract | 1. Freshly prepared hide-powder | The top horizontal column indicates the age of the preserved chromed hide-powder in days. | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | 1 day[1] | 2 days | 3 days | 4 days | 5 days | 6 days | 8 days | 10 days | 12 days | 14 days |
| Chestnut-extract..... | .0520 | .0500 | .0520 | .0520 | .0510 | .0520 | .0510 | .0510 | .0520 | .0500 | .0520 |
| Oakwood-extract .. | .0990 | .0990 | .0990 | .0990 | .1000 | .1010 | .0990 | .0990 | .0980 | .0990 | .0995 |
| Mimosa D . | .0720 | .0720 | .0710 | .0700 | .0720 | .0720 | .0710 | .0730 | .0720 | .0720 | .0720 |
| Sumac..... | .0980 | .0980 | .0980 | — | .0990 | — | .0980 | — | — | .0990 | .0980 |
| Quebracho-extract .. | .0250 | .0250 | .0230 | .0230 | .0250 | .0260 | .0250 | .0250 | .0250 | .0250 | .0240 |
| Myrabolam-extract .. | .1650 | .1650 | .1600 | .1640 | .1660 | .1650 | .1650 | .1640 | .1640 | .1660 | .1650 |

[1] 1 day = 24 hours.

Special attention is drawn to Column No. 1, which shows the results obtained with freshly prepared hide-powder according to the Official Method. It will be seen on comparing this column with the others that the results agree well within the limits of

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experimental error, even after the preserved powder has been standing for 14 days. No doubt boro-phenol will keep the powder in good condition for a much longer period, but for all practical purposes 14 days is sufficiently long.

In the above experiments American hide-powder was used, the authors having found this to be a most satisfactory powder. A similar series of experiments was carried out with Hungarian hide-powder, with equally satisfactory results. But the authors have had to discard the hide-powder obtained from the German Research Station. This powder prepared by Dr. Paessler has been found to contain a very high percentage of soluble matters, it swells up to an excessive degree, and it is practically impossible to wash it satisfactorily as prescribed by the rules of the I. A. L. T. C.

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## REVIEWS

**The Manufacture of Artificial Degras.** U. J. THUAU. *Le Cuir,* 1908, No. 2, pp. 15-16; No. 3, pp. 4-5; No. 4, pp. 8-9.—Degras is a general term applied to a series of fats easily emulsified with water, serving to curry leather. Originally the name was applied to the oxidized oils resulting from the chamois leather manufacture, today we have *moellon-degras pure, degras of commerce, degras mixtures, degras of fish-oil, olein-degras, black degras* and various forms of artificial degras which are more often mixtures of chemically oxidized oils.

Before studying the manufacture of artificial degras, something should be said of the nature of genuine degras. In the preparation of chamois leather, the hides are coated with fish-oil and after milling several hours are exposed to oxidation by the air, then alternately treated with fish-oil in the fulling apparatus to complete saturation. To complete the chemical transformation of the oil begun by the oxidation in air, the hides are allowed to ferment, they are placed in piles, care being taken to turn them occasionally.

*Moellon.*—Finally the hides are thrown into a cauldron of boiling water, and then the greater part of the fat is wrung out. The remaining water and oil is squeezed out in a hydraulic press. The liquid product from these two operations is called *moellon* or *moellon pure,* from hide; by decantation and heating most of its water can be separated.

*Degras.*—When the hides leave the hydraulic press they are soaked in a hot lye of carbonate of potash, 2.5° B., at 35° C., for one hour, and then wrung out. The alkali is then neutralized with a solution of dilute sulphuric acid, decomposing also any soap formed by the action of the potash on the oil absorbed by the hide. The oil which swims on the surface is degras or degras pure, from hide. After decantation, it is reheated with superheated steam to remove the greater part of the water.

*Degras of Commerce.*—The bleached oil known as moellon and degras pure, being insufficient for the demands of tanners, there are often added various animal fats (tallow), also divers fish-oils, etc. The mixture is very suitable for leather, provided that the added fatty material does not contain non-saponifiable matter which is too often the case. As it is, the thinned moellon-degras is very expensive when it contains much of the pure article, hence some *chamoiseurs* treat their hides with the sole object of producing moellon, soaking with oil and washing with alka-

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li repeatedly, using the hides over again to the extent of usury. The product thus obtained does not contain as much *degrasgene* (oxidized fat-acids) as pure moellon but sufficient to fix fatty matter upon the hide fiber.

*Degrasgene* is an oxidation product of fat-acids and like nearly all oxidation products (aldehydes, quinones, etc.), has a continuous tanning action. Simand (*Zeitschr. angew. Chem.*, 1891) treated samples of leather of different thicknesses with a moellon of known content of oxidized fat-acids; at the end of six weeks it was found that 66% of the fatty material combined with the leather was degrasgene. It is necessary, however, to take into account another fact, namely, that the fatty acids combined in fats (glycerides) may oxidize in contact with leather and a leather curried solely with fish or whale oil and exposed to oxidation, may contain after several weeks, considerable oxidized fat-acids combined with the hide fiber.

Good French degras should contain 10-12% of degrasgene (corresponding to 20% of water). In England, where the hides are piled longer, a content of 20% is reached, but the oil from the long exposure has abstracted nitrogenous matter from the hide which gives it a sirupy consistency and less penetrating power. Commercial degras therefore cannot be judged solely by its content of degrasgene; the free fatty acids should not reach 25% (calculated on anhydrous fatty substance) and there should not be over 3% of non-saponifiable fatty substances (mineral oils, resin oil, cholesterine, etc.).

As special articles will be published soon on the subject but one process of manufacture of commercial degras will be given. Freshly ignited lime is hydrated with a caustic soda solution of 25°B. 80 kilos of pale fish oil is boiled 1½ hours in a copper cauldron with 1 kilo of caustic lime from marble with constant agitation to avoid blackening from carbonization. When the liquid has become clear, it is strained through silk into a wooden vat; what has not filtered is mixed with water of 35° C. and returned to the sieve while incessantly agitating the contents of the vat until complete cooling. After some days 20 to 40 kilos of degras are added with agitation, then an intimate mixture (made at 40° in the cauldron) of 80 kilos refined suintine free from non-saponifiable matter, 30 kilos palm oil and 20 kilos of fish oil. The whole is agitated until cold and left to settle. If the mass remains fluid too hot water has been employed. After several hours a good commercial degras is obtained.

Compound degras may be classified between commercial and artificial degras; they contain a certain amount of pure moellon which however is too slight to perfectly curry the leather. The principal components are fish oil, oleine, bone oil, cotton-seed oil, etc.; resin oil, mineral oil, or resin are mere adulterations. According to one formula, 25 kilos of whale oil are heated to 80° and then 800 grams slaked lime mixed with a little water are added and well mixed; next are added 50 kilos moellon, 20 kilos refined suintine, 50 kilos palm oil and 20 liters

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water, with agitation till cold. A simpler formula requires 30 kilos whale oil, 5 kilos refined suintine, 15 kilos pure moellon, melted together at 80°.

What is known in trade as degras for leather dressing contains considerable tallow; it is somewhat difficult to attain a good mixing in its preparation. An example follows; 50 kilos moellon degras and 120 kilos whale oil are heated two hours at 80°, then filtered hot and 50 liters water and 600 grams ammonia added. Then 25 kilos tallow are melted in with stirring which is kept up to complete cooling.

*Artificial Degrases.*—These contain no moellon or degras, but certain oils and fatty substances oxidized or not by chemical means. They may be classified; (1) those containing suintine as base; (2) those containing fish oils as base; (3) degras of oleine, (4) degras from grease.

1. *Artificial Degras from Suintine.*—Suintine is a fatty coating from sheep's wool constituting 30%. There are two distinct operations in washing wool, (1) washing in pure water, removing soluble suintine; (2) degreasing, or washing with soap solution which gives the emulsion known as suint-fat or suintine. Suintine has a high power of emulsifying with water and resisting oxidation by the air does not become rancid. For this reason it is much used to adulterate degras and for the preparation of the artificial article. For an artificial degras, having the appearance of commercial degras although having but slight value for the currying of leather, it is sufficient to heat for two hours at 80° C. a mixture of suint and whale oil and after filtration the other ingredients are added to give body. The proportions used are:

| | Kilos | | Kilos |
|---|---|---|---|
| Suintine, purified | 20 | Suintine, crude | 40 |
| Whale oil | 20 | Whale oil | 20 |
| Mineral oil | 10 | Tallow | 5 |
| Tallow | 10 | Mineral oil | 5 |
| Palm oil, crude | 5 | Water | 25 |
| Water | 25 | | |

| | Kilos |
|---|---|
| Suintine, crude | 30 |
| Whale oil | 30 |
| Fish oil | 5 |
| Palm oil | 15 |
| Water | 20 |

2. *Artificial Degras with Fish Oil Base.*—

| | Kilos | | Kilos |
|---|---|---|---|
| Whale oil, oxidized | 20 | Whale oil, oxidized | 30 |
| Suintine, refined | 45 | Suintine, refined | 30 |
| Mineral oil | 7 | Mineral oil | 5 |
| Tallow | 3 | Tallow | 2 |
| Resin | 4 | Resin | 3 |
| Water | 20 | Water | 21 |

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| | Kilos | | Kilos |
|---|---|---|---|
| Whale oil, oxidized ..... | 45 | Whale oil, oxidized ..... | 65 |
| Suintine, refined..... | 25 | Suintine, refined..... | 10 |
| Mineral oil ..... | 4 | Fish grease..... | 6 |
| Tallow ..... | 4 | Water..... | 20 |
| Resin ..... ..... | 2 | | |
| Water..... | 20 | | |

Like those from suintine, these artificial degrases are of little value, their emulsifying with water being their sole recommendation for leather. The oxidized whale oil in these formulas is prepared in the same way as fish oil is sometimes oxidized before mixing with pure moellon from hide. Several processes are in vogue. In the Livaché process fish oil is agitated with finely divided lead which has been obtained by precipitating a solution of nitrate of lead and nitrate of manganese with plates of zinc, all in presence of the oil. After decantation, the oil is agitated with oxide of lead, thus decomposing the excess of nitrate of manganese. In the German process fish oil is heated to 80° and 3% of nitric acid of 36° B. incorporated; after reaction is over, the excess of acid is neutralized with ammonia. A physical process employed consists in allowing the oil to flow from a reservoir placed in the top of a tower down upon a perforated plate through which are suspended threads; the oil trickles down these upon a second plate and finally runs into a reservoir, a current of air at 50° circulating over the upper plate. Good oxidation requires three or four passages of the oil. Another process consists in heating at 40° a mixture of cod-liver oil and suintine with hydrogen peroxide agitating several hours with compressed air at 2 atmospheres.

**Uniformity of Tan Liquors.** Address by L. Manstetten. *Gerber Zeitung*, 1908, 23, 24, 30.—This depends upon three factors, (1) uniformity of original material, (2) uniformity in preparation, (3) uniformity in employment. (1) The first is very difficult to maintain, and requires a sharp control of the purchased material. Besides the tan-stuffs and acid in a liquor, the non-tans remaining after fermentation of the sugar substances to acids, have an influence; two practical examples show this. The old vat liquors from the preliminary tannage in many upper-leather tanneries although containing sufficient acid, plump the leather but little; this is explained by the retarding influence of accumulated unfermentable non-tans. In one tannery, the sole-leather vats contained 0.3-0.4% acid and the leather was well plumped; the old upper-leather vats contained 0.5-0.6% acid, yet there was little swelling. That the non-tans restrain the plumping can be shown by increasing their amount by the addition of salt when the plumping is still further decreased. In the so-called pickle, salt is added to the acid to hinder plumping.

It is not economical in practice to employ always the same tanning material because of market conditions. Accordingly the term uniformity

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as used here is based upon uniform tanning effect rather than absolute uniform composition. To produce a uniform working liquor we must consider (a) the nature of the tan-stuffs and acids present, (b) the ratio of tan-stuffs to acids, (c) the ratio of tans plus acids to the remaining solubles. An illustration of (b) is taken from the speaker's practice. Formerly in the Leather School (Frieberg) the vache-leather vats had been strengthened by adding to each 1-2 liters acetic acid and several buckets of fresh liquor, raising the acid content to 1% and higher; nevertheless the hides were but moderately swelled, the action of the acid being retarded by the fresh liquor. On reducing the acid one-half and especially on keeping the lower vats proportionately poorer in tan, a much better plumping was obtained.

(2) Uniformity in preparation is not so simple as it might seem; at times uniform unalterable methods may themselves lead to variations in the liquors. An essential factor in the efficiency of a liquor is the employment of spent liquors for leaching. This is not good practice if a well plumped leather is demanded. Another evil which the employment of spent liquors brings about in many cases is pointed out. It is of course excluded that the old liquor will suffice for the preparation of sufficient fresh for operation consequently a portion must be made with fresh water. Two different liquors therefore result unless a mixture be made according to some uniform rule. Resort is often had to employment of the separate liquors for varied processes to which they are suited. Errors may thereby occur, for they cannot be valued by gravity determination since the accumulated non-tans raise the gravity disproportionately. The slow tannage so often complained of in such cases is due not only to weakness in tan but also to the retarding effected by excessive non-tans. These principles have been well demonstrated by Paessler (*Gerber Zeitung, Jahrg.*, 29).

It is often the practice in leaching to withdraw successive liquors from the leaches for separate uses the assumption being that all are of the same relative composition, the last being merely weaker.

This is not the case at all; the last extraction (promoted by heat) contains the less soluble tans. Also the proportion of non-tans consist largely of easily soluble saccharine substances is greater in the first extracts. An extraction experiment made with pine bark shows this, a sample being leached first with 1 liter cold water, then with 1 liter hot (100° C.) in Koch's extraction apparatus.

| | Cold | Hot |
|---|---|---|
| Total extract | 13.55% | 6.0% |
| Tan-stuffs | 8.11% | 4.8% |
| Non-tans | 5.44% | 1.2% |
| Incl. sugars | 2.42% | 0.37% |

or for 100 parts tan-stuffs:

| | Parts | Parts |
|---|---|---|
| Non-tans | 67.0 | 25.0 |
| Sugars, incl. | 29.8 | 7.7 |

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An extraction was then made on a larger scale in a copper extraction apparatus using here relatively less water, just sufficient to cover the bark. The same material gave

| | Cold (14°C.) | Warm (60°) | Hot (100°) |
|---|---|---|---|
| **Total extract** | 1.25 | 1.19 | 1.95 |
| **Tan-stuffs** | 0.48 | 0.51 | 1.28 |
| **Non-tans** | 0.87 | 0.68 | 0.67 |
| **Incl. sugars** | 0.53 | 0.34 | 0.20 |
| **or for 100 parts tan-stuffs:** | | | |
| **Non-tans** | 180.1 | 133.3 | 52.3 |
| **Sugars, incl.** | 110.4 | 66.7 | 15.5 |

These results which may be applied to direct practice, depend first of all upon the amount of water used. Nevertheless, they show that the non-tans (at least in pine) to be more soluble than the tans. This also has a bearing in the employment of layaway bark. The liquor will be rich in non-tans and the recovered bark, the so-called sour-bark proportionately poor. This bark may still show considerable differences on repeated extractions. From a leach filled chiefly with recovered layaway bark with some hemlock, mimosa and myrabolams, the first extract of 4° B. gave 17.5 parts sugars to 100 parts tan; the second extract of 3° B. gave only 13.6 parts non-tans. The foregoing shows that a liquor may vary greatly according to the method of preparation. In practice the speaker has found in different tanneries making the same sort of leather, liquors containing for 100 parts of tan-stuffs, 10.2 to 5.5 non-tans.

(3) Uniformity in application is just as essential as in the composition and preparation of liquors. For example, it is not correct as is often done to use the strong liquors irregularly without regard to source and adjust the tan-vats by the barkometer. Specific gravity determinations cannot show the character of liquors differently prepared and used, although they may be used for control when the processes are uniformly maintained. Neglect of these facts has undoubtedly led in many cases to variations in leather obtained by an apparently uniform process.

The relative amounts of acid contained in the consecutive tan-vats of a tan-yard depend upon the process followed. If in each vat the acid content is the same, it shows the hides have received a preliminary plumping in a special bath and take up no more acid. If the acid content remains the same in the upper vats and falls off in the lower, then acid liquor has been used and the butts have not been previously plumped. If the acid amounts increase in the upper parts from the last towards the middle and then remains constant, more or less fresh liquor has been used, and plumped hides introduced. Finally, if the acid increases towards the middle layer and then falls off, more or less sweet liquor has been used and the hides have not been plumped.

**The Removal of Spots from White Leather.** *Gerber Zeitung,* 1908.—The lighter spots are best removed by alcohol as this does not dissolve the tan and bring about a hardening of the leather. Rubbing with a rag is gen-

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erally best, but with large spots it is necessary to completely soften and wash the grain with a thin paste of wheat meal, the yolks of two or three eggs and one-half liter of water to which finally some alum is added. The leather can also be thoroughly washed in lukewarm water and obstinate spots removed by ammonia or very dilute acid followed by a thorough washing and rubbing with the above paste. In this case after drying, stretching and re-currying are necessary which makes this process unprofitable in most cases. Some recommend thick soap solution for cleansing white leather which at the same time leaves a handsome gloss.

**Frauds in Crude Hides.** (Current). *Le Cuir*, 1908, No. 4, pp. 17-19.—The question of fraud and poor rendement in crude hides merits study, for tanners often complain of gains below the average. When the hides are in process of manufacture, it is impossible to make reclamation and it is necessary that tanners should be able to avoid deception or at least have their eyes open to the situation. The faults which may occasion a yield less than expected are diverse; the principal ones are loss of weight in transit, injuries to the grain of the leather as a result of prolonged exposure to moist heat, contact with harmful substances; for all hides, but particularly for small ones, bad drying, preventing restoration to original state on softening, numberless defects in skinning, holes, gashes, etc., concealed defects in grain caused by disease in the animal or by the goads of drivers or by parasites; finally intentional frauds made by the butchers or dealers. A campaign is now being carried out among the European states in the interests of tanners to secure a better quality of hides in the domestic and foreign markets.

The voluntary frauds are of the most importance in this discussion and consist always in some overweighting of the hides with foreign substances, sometimes water which is easily perceived by one of the trade, sometimes with foreign matters added to the hides with the salt. In this case it is difficult or even impossible for the tanner to discover the fraud by simple inspection. There is however a means of recognition namely chemical analysis. There are average figures known representing the quantity of salt a well salted hide should contain, also the water; above all chemical analysis can detect any foreign materials. If the tanner has doubts of his crude hides nothing is easier than to assure himself by having this examination made. While this cannot be done for each small lot of hides, it ought to be done when the source of supply is changed or when a large quantity is handled. The increase in the cost of material will be recovered on the ultimate discovery of fraud.

How may the tanner be led to suspect fraud? The rendement will show him. Those who make their calculations irregularly or not at all as is too often the case, may be easily deceived; it is otherwise with the tanner who keeps exact records at all stages of operation; on finishing work, or even before tannage he will be able to detect fraud. The verification of fraud is based with greater certainty upon the rendement in the white weight than that in finished leather. It is simply a question of comparing the weights with that of the crude hides and accounting

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for the difference. This comparison however may be made in different terms, namely:

(1) The weight of salted hides may be compared with that of fresh hides; this last is not generally known by the tanner but there is a method of ascertaining it by inspection of the salted hides which will later be recurred to.

(2) The weight of the salted hides may be compared with their weights after once soaking; the results may be compared with figures established by practice.

(3) Finally, the weight of the salted hides may be compared with that of the white weight, that is, the weight of the cleaned hides freed from impurities, hair, salt, etc. This last method is the one oftenest employed and gives the most certain results.

**Metric Measurement of Leather in Austria.** *Der Gerber.*, 1908, No. 804, p. 62.—At a meeting of the leather dealers of Vienna, the question of English vs. metric measurement was vigorously discussed, both methods finding support. For foreign and some divisions of domestic trade the English foot is demanded. Measuring machines such as Corradi's which give metric readings can be controlled directly by the user who is familiar with this scale. It was voted by a large majority that metric measurement ought to be official and that the government be petitioned to verify standard instruments.

**An Adulteration of Tan Extracts.** *Le Cuir.*, 1908, through *Collegium*, 1908, p. 124.—To reduce the precipitation of difficultly soluble tannic anhydrides (phlobaphenes) in the concentration of tan extracts, manufacturers employ alkaline bisulphites. The writer believes, notwithstanding the assertions of some authors, that the sulphurous acid becomes oxidized to sulphuric acid in the leather to the detriment of the latter. As for the substitution of sodium carbonate or borax, this causes browning, the oxidation of tans in the presence of alkali being very rapid, the darkening being similar to the familiar reaction of alkaline solutions of pyrogallol.

**The Installation of Open Leaches for Leaching Vegetable Tanning Materials.** L. MANSTETTEN. *Frieberg Tanners' School Report, through Gerber Zeitung.*, 1908 [51], Nos. 85, 93-4, 95-6, 112.—Although the majority of tanners still employ this method, the author prefers extraction without superheating in closed vessels, and before entering on his main theme describes the satisfactory performance of a recently introduced extraction apparatus, Rieder's "Automat." Experiments with an inferior pine bark of 9.4% tans gave a liquor of 3.0° B., reducing the bark to 2.4% tans. A mixture of 6 parts of same pine bark, 2 parts malett and 1 part Dividivi, gave a liquor of 7.0° B., with spent bark of 2.5%.

In the use of open leaches, both single vats and a series of several, a section are employed which is the preferable arrangement and the only one described here. The number of vats in a section run from 2 to 8; 4 is the lowest advisable number for efficiency.

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Generally the liquor is not pumped from leach to leach but transferred automatically on the principle of communicating tubes. One part of the tube is the vat itself filled with bark and liquor, the other end is an inner vertical wooden log called the press log into which the liquor can only enter from the bottom and issues at the top passing to the next leach by a communicating log. In the next leach the same process is repeated; as the liquor flows in at the top, that at the bottom is pressed upward through the press log, flowing over to the next leach and so on. That there is very little mixing during this circulation can be demonstrated by cautiously flowing cold water into the top of a warm leach; the temperature of the issuing liquid is not much lowered until the hot liquid has been nearly displaced. The continuous displacement of liquid in this process is called technically, pressing over. The leaching out is effected by allowing water to flow into the last leach of the section which contains the nearly spent bark, the liquor flowing thence into the next leach containing the next less extracted bark; the weak liquor proceeds thence through the successive leaches until it is finally drawn off for use from the vat containing fresh bark; when a sufficient amount of this strongest liquor is obtained and the poorest bark is sufficiently extracted (generally with heat), this is removed, replaced by fresh bark, and the next following poorer bark treated with water, beginning a new cycle.

The best constructed leaches are bound with iron hoops and are conical in form, widest at the bottom; to save room, instead of circular, a square section is employed, the corners being leveled. When possible it is preferable to set leaches in the ground, bedded in mortar or clay. The upper edges must be accurately at the same level to ensure efficient circulation. Each pit is set plumb and care should be taken that the bottom is uniformly supported. Leaches are provided with a false bottom, the lower chamber being 6 to 10 inches deep. The construction of this partition is important since it supports the bark and separates it from clear liquor. It is sometimes perforated with round holes which is not to be recommended, since these easily plug up if too small, and let bark through if too large. A close lattice of slats of triangular section is also used but requires frequent cleaning. The best arrangement is to simply lay narrow boards cut on a bevel beside each other without close fitting; the channels which form allow sufficient liquor to pass and do not easily clog. The press log which is built against an inner wall of the pit may be of square or triangular section accordingly as made of three or two boards, or even one board suffices to close up a triangular tube in a corner of a square leach. The joints should be absolutely tight, allowing no communication with the leach above the false bottom, else the circulation would be vitiated. The lower ends of the boards are notched sawtooth fashion to allow the liquor from the lower chamber to enter the press log. It is utterly bad practice to bore holes in the press log above the false bottom as is sometimes done as this cuts out more or less of the pit from circulation. Heed should be taken that liquor enters the press log only from below after first circulating through the bark and

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not to be admitted from the top. An illustration of such false installation is given by the writer. Another fault consists in placing the communication from pit to pit directly in the upper edge; it should be 6 to 8 inches lower, permitting a slight back pressure which accelerates the circulation.

It is not advisable to place the leaches of a section in one line, but better to arrange an even number in two parallel rows, thereby shortening the connections. An advantage of a circular arrangement is that all the conduits for each group of four leaches may be brought together in the center for convenience in connecting with any leach of the section. The leaches themselves are best connected by copper pipes; valves in these are an unnecessary expense, a simple wooden plug serving to shut off any pit.

It is the usual practice to heat the pits containing the last extractions with steam; this is introduced directly or indirectly through copper coils. The writer does not consider direct steam so injurious to the tan as some think; the condensation is immediate and the agitation is of advantage. The position of the heating coil is important; it is often placed beneath the false bottom, with a view to avoid heating the bark too directly. According to the writer's experience, the best results are obtained with the coils above the false bottom. A section of leaches with the steam coils beneath required complete cleaning out after each finished extraction. On placing the heating arrangement above, it was found that much less bark went through the partition, needing removal only four times a year. Steam was saved and a much better loosening of the bark during extraction resulted. An objection to the lower position of the coil is that the liquor beneath must be brought to vigorous boiling in order to heat the extraction mass above the partition, thereby requiring increased pressure of steam. An arrangement often used for agitating leaches shows that these conditions are present. A vertical copper pipe, open at each end, passes down the centre of the pit through the partition to the bottom; here the liquor heated by the steam coil boils actively and is driven up through the pipe falling back on the bark. Such an arrangement has the disadvantage of agitating the hot liquor in the air which darkens it greatly as may be proved by boiling a sample of clear liquor in the air; it will also be found that a portion of the dissolved substances, mostly tans, become insoluble.

Another device used for heating and agitating is the steam-blast elevator or injector which is quite efficient. If the injector is placed above the pit, the extraction cannot be heated above 80° C., as the suction then ceases. This can be helped by placing the apparatus at the bottom of the pit. In any case the elevated hot liquor should be conducted back to the pit through a pipe or hose without contact with air to avoid darkening.

**A Study of Tanning Extracts.** (Current). U. J. THUAU. *Le Cuir*, 1908, No. 2, pp. 7-8; No. 3, pp. 19-20.—Sulphited extracts are used in greatest quantity. Extracts of quebracho, mangrove and hemlock contain difficultly soluble ingredients which dissolve however in presence of bisulphites, giving the cold soluble extracts of commerce. Also the bark itself

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may be treated with bisulphites. Sulphited extracts may be divided into two classes, (1) those containing free sulphurous acid, (2) those which do not. The last penetrate the hide very easily, giving a very clear leather. The first penetrate even more easily, but the combination with the fiber is not as stable as with the second class, or with non-sulphited extracts, and are extractable with water. The best method of using sulphited extracts is to fix them upon the fiber by the acid of other tanning materials which then increase the rendement. For instance in a tannage of sole-leather by the rapid process it would be advantageous to begin (assuming that the hides have been chemically delimed) by treatment with sulphited quebracho followed by ¾ chestnut and ¼ quebracho, then chestnut alone finishing with non-sulphited chestnut. This gives the best rendement of all rapid processes. However, many English tanners prefer to finish with sulphited chestnut; a very concentrated and hot liquor is employed from a sulphited extract called "Bleaching Extract."

Quebracho wood contains 20% tannin, 1.5% non-tannin, 64% insoluble, 14.5% water. The non-tannin includes 0.25% sugar, or 1.2 parts sugar to 100 parts tannin, while in chestnut wood there are 9.3 parts sugar to 100 of tannin. This explains the greater susceptibility of chestnut extract liquor to fermentation.

There are three types of quebracho extract in commerce, (1) clarified extracts, which contain nevertheless much insolubles, (2) decolorized extracts, (3) cold soluble extracts. Of the first, in various strengths, average analyses give:

| | Liquid, 23° B. | Thick, 27° B. | Solid |
|---|---|---|---|
| Tannin | 35 | 40 | 65 |
| Non-tannin | 4 | 5 | 7 |
| Insoluble | 3 | 5 | 8 |
| Water | 58 | 50 | 20 |
| Ash | 0.5 | 0.7 | 1 |

The decolorized extracts, slightly sulphited, soluble with heat give:

| | Liquid | Solid, crystallized |
|---|---|---|
| Tannin | 39.5 | 73.6 |
| Non-tannin | 5.1 | 13.4 |
| Insoluble | 0.3 | 0.2 |
| Water | 55.1 | 12.8 |
| Ash | 0.8 | 5.7 |

The third class, the most sulphited, are soluble in the cold.

| | Liquid, 22.5° B. | Thick, 28° B. | Solid |
|---|---|---|---|
| Tannin | 36.0 | 43.0 | 69.0 |
| Non-tannin | 4.0 | 4.5 | 11.0 |
| Insoluble | 0.0 | 0.0 | 0.0 |
| Water | 60.0 | 50.0 | 20.0 |
| Ash | 2.3 | 2.4 | 7.0 |

Quebracho extract, sulphited or not, is seldom employed alone; it has a marked power (especially when sulphited), of penetrating the hide

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rapidly but gives a lax leather, therefore it is always mixed with extracts of chestnut, oak, etc. It is only employed alone for horse-hides and even then 1 to 4 % alum is added.

*Manufacture of Sulphited Extracts.*—The process of Lepetit, Dollfus and Gansser (1896) was the first practical one. They operated in three ways; (a) heating in an autoclave for 6 hours at 140-150° C., 300 kilos extract of quebracho of 25° B., with 80 kilos bisulphite soda of 35° B., (b) heating by steam at 1½-3 atmospheres in a jacketed kettle provided with an agitator, 300 kilos extract of quebracho, and 100 kilos of bisulphite or neutral sulphite of soda of 30° B., or 130 kilos of hydrosulphite of soda of 20° B.; (c) instead of using extract, the wood itself was extracted, with or without pressure, adding for 100 kilos of quebracho wood, 12-15 kilos bisulphite or sulphite to the water. The sulphites of ammonia and potash were also substituted. They also found later that soluble extracts could be obtained by employing other alkaline salts such as borax, carbonates, bicarbonates, phosphates, lactates, sulphides and also hydroxides. In this case heat is still required to make the solution, but the operation is effected much more rapidly than with sulphites. The product however is not so useful to the tanner for a good extract should contain neither free base or acid.

**A Tan Extract Suit.** (Steiner Bros.). *Der Gerber*, 1908, No. 809, pp. 133-5.—This firm operating a tannery in Graz publishes a caustic protest against the sale of blended quebracho extracts as pure and describes its experiences. When mangrove first came into the market, it was given a trial and found to be utterly useless for the kind of work required, the production of russet leather which must have a light colored grain and little grease. Mimosa D extract, a sulphited quebracho extract was used several years, but gave too little body to the leather. Accordingly quebracho extract was purchased of Oesinger's manufacture, which was guaranteed without admixture. This extract was used 2½ years with unsatisfactory results, giving dark colored, hard and brittle leather with splits, and only tanning the surfaces of thicker hides, often necessitating splitting to tan the inside. It was then learned that this extract was blended with mangrove and myrabolams as confirmed by actual analysis at the Vienna Station. Although Freiberg reported no admixture, with the proviso that small amounts of mangrove cannot be detected. A legal suit was instituted but finally compromised in favor of the consumers.

Inquiry showed that of other factories using this brand of extract, 8 had trouble and 3 were satisfied. Many of the troubles experienced by tanners in these times are attributed to the mischievous blending of extracts. One remarkable example is cited as occurring in a large leather factory; on completion of a tannage *twice* as many skins were taken out of the drum as were put in. The explanation is, that the surfaces only were tanned, the interior heated, became glue and the rolling split the hides. An American quebracho extract, guaranteed, sent to the Vienna station showed mixture with myrabolams. In conclusion, the only resort for the tanner seems to be to make his own extracts.

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**Remarks on a Tan Extract Suit.** W. EITNER. *Der Gerber*, 1908, No. 810, pp. 147-9.—Since the publication of the writer's article of last year on "Blended Extracts," there has been no improvement in the general situation. All the present differences between extract dealers and consumers relate to quebracho. This tan-stuff has the power of rapidly and thoroughly tanning the leather through and further of making it full, firm and heavy, other admixed materials affecting more or less the color. Although desirable, the extract makers pay no attention to making different brands suited to special purposes. The distinctions are based solely on consistency, tan contents, and solubility and not at all on purity which is precisely what is of importance in use. The mixing should be the affair of the tanner.

The present situation in the sole-leather industry forces the tanner to seek high rendement in weight by impregnation with the ordinary weighting materials or with tan extracts. The usual loading materials, starch products, barium, Epsom and Glauber salts can be completely washed out of leather by water, while leather containing the extracts used for filling and weighting do not have this disagreeable property. Quebracho extract possesses this filling property in a high degree but is expensive used in this way as it cannot be prepared to suit these conditions; it is therefore mixed with cheaper substitutes. This is on a par with weighting leather and to the same extent legitimate. Quebracho blended with mangrove and myrabolams is better suited for filling leather by an after tannage than pure Argentine quebracho extract itself, because more soluble. For this purpose then quebracho extract is necessarily blended and is only impure when foreign substances like sugar, etc., are added for cheapening and giving consistency.

This is not the case however, when quebracho is to be used for tanning proper. The experiences of Steiner Bros. (leading to the suit referred to in title) confirm all the authors remarks on the injurious action of mangrove published in the article on "Blended Extracts." The extract makers should stand by his guarantee of purity.

The following standard types of manufactured quebracho extracts as suited to various purposes are proposed:

(1) Easily soluble, not sulphited, guaranteed pure, from quebracho wood.

(2) (a) Same, sulphited.

(b) Sulphited, easily soluble, without guarantee.

(3) (a) Natural, therefore not clear soluble extract, guaranteed pure.

(b) Natural, not clear soluble, without guarantee.

These would satisfy all the needs of tanners; instructions for use would be desirable.

As to the tan contents guarantee so much discussed, this is irrelevant when the extract is to be used for filling, quality counting here. For real tanning, the amount of tan is the main factor, but not the sole one, for the nature of the tan-stuff is of consequence; hence a quebracho extract cannot be judged by its guaranteed tan contents.

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**Design for a Chrome Leather Factory.** O. ZENKER. *Gerber Zeitung*, 1908.—The vertical style is only to be chosen in cities; elsewhere the horizontal style is preferable. In this design (illustrated by 2 floor-plans) the crude hides are unloaded on the ground floor in the center of the building and thence transferred to the adjoining room to the soaking-tanks, next day stretched on the machines, then to the reel-soaks, till next day in flowing water; next to the limes (also reeled). Then follow machines for preparing the skins and finally the room containing the drums or wheels for rinsing, bating, hair washing, tanning and washing out. These are all of one size, in a line, driven by one shaft from the rear; the driving pinions on this shaft may be slid to engage with the teeth on the drum, the whole arrangement being compact and noiseless. Above the row of drums is a gallery upon which the hides are brought by hand cars from the elevator at the end and dropped beneath into the proper drum. When a drum is emptied an open car of lattice work is placed beneath; filling and emptying require but a few minutes. The gallery, 12 ft. high and 12 ft. broad also serves to support the vessels for mixing and storing the chemicals which are supplied by pipes to the tanning drums, permitting accurate work. Near by, are 10 reel vats for the after tannage with bark.

On the second floor where the leather is finished, a large drying room occupies the centre and the surrounding rooms contain the various machines, etc., arranged in order of operation. The plans call for a height of 21 ft. for the ground story and 18 ft. for the upper. Windows are recommended to be placed high and the frequent present factory style of extension to the floor is deprecated as unsightly and useless.

**Blood-Glaze for Leather.** *Gerber Zeitung*, 1908.—Blood-glaze for brush application must have a higher gloss than that applied as polish where the shine is developed by pressure and rubbing. The active ingredient is the blood albumen, and to increase the gloss, more blood must be used or some other albumen as white of egg, may be added. A very good glaze may be obtained by adding a moderately thick glue solution to blood. Addition of sugar is also favorable. Three liters pure ox-blood mixed with ¼ liter good spirit makes also a good mixture; this must be well beaten. The offensive odor of the blood is overcome by the alcohol, which being antiseptic preserves the mixture for some time. A black may be obtained by the addition of nigrosine.

**Loss of Tannin in Leaching.** (Current). *Le Cuir*, 1908, No. 2, pp. 1-3. —The preceding article on this subject appears to have aroused much interest among tanners, many samples for analysis having been sent in to the laboratory As a typical example, analyses of two samples of (so-called) spent bark from one of the foremost French tanneries are given:

| | I. | II. |
|---|---|---|
| **Tannin** | 3.3 | 3.7 |
| **Non-tannin** | 1.0 | 1.2 |
| **Insoluble** | 81.4 | 80.3 |
| **Water** | 14.3 | 14.8 |

(*International Method*).

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A complete extraction of the bark would give cloudy liquor and bad color to the leather, but one ought to extract down to 1½% without affecting the quality of the leather. Eighteen to 20 kilos of tannin (22 to 25 francs) for every 1000 kilos of oak bark are lost; this is a frequent condition. The remedy for this is a rational extraction process; solution is promoted by agitation and heat, particularly the last. With cold extraction, oak is never completely exhausted. Scientific research has shown that for each tanning material, there is a critical temperature beyond which it is not possible to obtain a clear extract free from coloring matter and non-tans injurious to leather. This temperature for oak-bark is 80° C. By heating progressively in open pits up to 80° the portion soluble in cold at 15° by the old process is obtained and in addition that which dissolves from 15-80° and is still excellent for tanning. Many tanners have rejected hot extraction because precipitates have been obtained; this is due to heating above the critical temperature.

**Extracts from the Annual Report of the Freiberg Versuchsanstalt für Leder Industrie.** *Gerber Zeitung*, 1908.—The analysis of tanning materials from Aug. 15 to close of 1907 was carried out by both the old and the new methods. It is believed that as the shake-method becomes more familiar, more concordant results will be obtained in general practice. The concensus of all reports show a lower content of tan-stuffs by this method. In this report the old method is understood to be used unless otherwise stated.

| | Oak-bark | | Pine-bark | | Mimosa-bark | | Mangrove-bark | |
|---|---|---|---|---|---|---|---|---|
| Samples..... | 67 | | 80 | | 38 | | 26 | |
| | Mean | Limits | Mean | Limits | Mean | Limits | Mean | Limits |
| Filter-method: | | | | | | | | |
| Tan-stuffs .... | 11.4 | 7.8-15.5 | 12.3 | 7.7-16.6 | 33.6 | 24.1-43.1 | 37.5 | 19.0-49.6 |
| Soluble non-tannins..... | 6.0 | | 8.6 | | 9.8 | | 8.4 | |
| Insolubles .... | 70.9 | | 65.7 | | 44.2 | | 39.4 | |
| Water ..... | 11.7 | | 13.4 | | 12.4 | | 14.7 | |
| Shake-method: | | | | | | | | |
| Tan-stuffs .... | 10.2 | | 10.6 | | 31.5 | | 34.7 | |
| Difference (less) ..... | 1.2 | | 1.7 | | 2.1 | | 2.8 | |

| | Mallet-bark | | Valonea | | Trillo | | Myrabolams | |
|---|---|---|---|---|---|---|---|---|
| Samples..... | 48 | | 14 | | 86 | | 12 | |
| | Mean | Limits | Mean | Limits | Mean | Limits | Mean | Limits |
| Filter-method: | | | | | | | | |
| Tan-stuffs .... | 42.9 | 37.9-49.6 | 32.1 | 27.6-36.0 | 42.5 | 34.8-48.1 | 36.6 | 29.9.42.7 |
| Soluble non-tannins..... | 8.0 | | 11.7 | | 13.3 | | 11.2 | |
| Insolubles .... | 36.3 | | 43.7 | | 31.7 | | 42.8 | |
| Water..... | 12.8 | | 12.5 | | 12.5 | | 9.4 | |
| Shake-method: | | | | | | | | |
| Tan-stuffs .... | 38.9 | | 29.4 | | 38.6 | | 30.5 | |
| Difference (less) ..... | 4.0 | | 2.7 | | 3.9 | | 6.1 | |

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| | Myrabolams, seeded | | Oak-galls | | Quebracho wood | | Sumac | |
|---|---|---|---|---|---|---|---|---|
| Samples..... | 9 | | 4 | | 22 | | 128 | |
| | Mean | Limits | Mean | Limits | Mean | Limits | Mean | Limits |
| Filter-method: | | | | | | | | |
| Tan-stuffs .... | 50.5 | 47.2-53.0 | 34.0 | 32.7-35.5 | 20.9 | 13.5-24.3 | 25.0 | 16.2-32.7 |
| Soluble non-tannins..... | 17.7 | | 6.5 | | 1.6 | | 16.3 | |
| Insolubles .... | 20.7 | | 46.2 | | 63.3 | | 49.5 | |
| Water ..... | 11.1 | | 13.3 | | 14.2 | | 9.2 | |
| Shake-method: | | | | | | | | |
| Tan-stuffs .... | | | | | 19.3 | | 22.6 | |
| Difference (less) | | | | | 1.6 | | 2.4 | |

The mallet bark analyses show that this material is seldom adulterated as represented in the trade journals. Trillo is also now but little adulterated. Sumac which was sent in largest amounts appeared to be pure for the most part; one sample analyzing low (16.2%) showed an excessive amount of leaf-stems.

In addition, the analysis of chestnut wood is given as water 14.5%, tan-stuffs 6.8 to 15.1% whereas oak-wood gave 4 to 6% tans.

Of the extracts sent in quebracho wood extract showed 2.8% lower tan-stuffs by the shake-method. 450 samples chestnut-wood extract were normal, 24-27° B.; 28-30° extracts are now seldom sold and solid extract not at all. 3.3% lower tan-stuffs were found by the shake-method. Of the extracts sent in designated quebracho (1300 samples), few represented pure quebracho, but were for the most part mixtures which show great variations. With pure quebracho extracts of 30-40% tans, differences of 1.3 to 3% may be expected by the shake-method, and for the solid extract, 2 to 4%; greater differences indicate mixed extracts.

| | Pine extract | Mimosa extract | Mangrove extract | Myrabolam extract | Sumac extract |
|---|---|---|---|---|---|
| Number samples..... | 18 | 9 | 5 | 7 | 6 |
| Tan-stuffs..... | 16.4-26.0 | 25.3-36.6 | 31.6-34.5 | 25.4-32.0 | 14.9-27.0 |
| Water ..... | 69.4-56.5 | 62.8-50.2 | 58.8-56.9 | 61.7-50.3 | 74.2-53.4 |
| Specif. grav. B° ..... | | 23.1-29.7 | 23.3.24.0 | 24.1-30.4 | 15.9-29.5 |
| Less tans., by shake-method ..... | 3.4 | 3.2 | | | |

"Extract Mimosa D" is not a mimosa extract, but cold soluble quebracho extract; it can be recognized by its high ash (from sulphites;), 4.4 to 7.1% while genuine mimosa has an ash of 1 to 2%.

Many samples of fat were sent in. Some samples of moellon gave 16.2 to 32.2% vaseline which is beyond what is allowable to give proper consistence; the highest water content was 20.5 to 31.8%. One sample "Degras" gave 41.0% insoluble in petroleum ether (sugar), 32.2% mineral oil, 9.0% saponified. One sample moellon gave 4.0% ash incl. 3.86% barium chloride. Some fish oils showed 78.5% mineral oils.

Samples of leather showed at times considerable loading; vache leathers contained 2.9 to 10.6% sugar, 9.6% $BaCl_2$; 5.1% $BaSO_4$. One vache

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leather of the high gravity 1.228 contained 18.1% extractable; this was due to impregnation with strong tannage. Many leathers were loaded with fat, belting 27.2%, horse-leathers 36.4%, harness leather 38.5%. Belting leather sent in to ascertain cause of easy tearing showed the fat content (17.4-18.3%) to be 75-78% fatty acids. Several cases of weakness in leather were attributed to iron (0.8-1.5% $Fe_2O_3$).

Leather dressings for the most part proved to be made of materials used to weight leather; one contained 15% glucose, 58% dextrine, another, 14% dextrine, 24% magnesium chloride. If employed in excessive amounts, the consumer might be suspected of intentional loading.

**Loss of Tannin in Waste Liquor.** *Le Cuir*, 1908, No. 3, pp. 1-2; No. 4, pp. 1-2.—Tan may also be wasted in the liquor which has been through the operations of tanning, particularly vat tannage. This is illustrated by the following analysis which as well as previous analyses quoted were made in the laboratory of *La Cuir*. The first example, a liquor from the tannage of splits gave:

| | |
|---|---|
| **Tannin** | 2.5 |
| **Non-tannin** | 13.9 (**acid**, 1.4 **gms. to liter**) |
| **Insoluble** | 0.0 |
| **Water** | 83.6 |

which represents a loss of 25 to 30 francs to each cubic meter. In another tannery where the tanning is carried out in vats with liquors made from extracts, the liquors are pumped from vat to vat, one vat always remaining empty for the preparation of strong liquor. The waste liquor analyzed

| | |
|---|---|
| **Tannin** | 3.3 |
| **Non-tannin** | 11.8 (**acid**, 2.2 **gms. to liter**) |
| **Insoluble** | 0.1 |
| **Water** | 84.8 |

Some tanners seek to prevent these losses by using old liquors for the preparation of new, but this does not make for good and regular tannage. When the liquor has been employed a certain number of times, it contains besides fermentation acids, a considerable amount of non-tannins; as these increase, they injure the bloom, structure and color of the leather and in addition retard the action of tannin itself. The old liquors therefore cannot be retained indefinitely. The two analyses quoted show that the liquor did not contain too much acid and was moreover very clear. It is certain that much of the tannin still present could be utilized by adding a portion to the head vat and also by exhausting it further by the butts as they enter tannage.

The waste liquor reported above as still containing 3.3% tannins, came from a tannery using a yard of 28 vats. In the meantime the advice given in the preceding paragraph has been followed by this and other tanneries with most satisfactory results. Instead of using pure water for preparing new liquor, the weakest liquor of the preceding tannage has been used instead of sending it to the river; since it contained

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3.3%, only sufficient extract was taken to yield 11.7%, to make up to the 15% finally required. This new liquor, made up from the old liquor (A) on making the round again gave the analysis shown under (B):

| | (A) | (B) |
|---|---|---|
| Tannin | 3.3 | 0.5 |
| Non-tannin | 11.8 | 1.8 |
| Insoluble | 0.1 | 0.2 |
| Water | 84.8 | 97.5 |

In this tannery, one of the best in the Paris region, it has been decided to use the liquor three times in succession; after this the old liquor becomes too fermented to produce regular tannage. With this altered process, the leather has been of as good quality as formerly and the economical result has been a saving of 800 francs monthly.

**Loss of Hide in Soaking.** *Le Cuir*, 1908, No. 3, pp. 2-4; No. 4, p. 3. The object of this treatment in the case of fresh skins is a mere washing which should not be prolonged beyond the time needed to remove the impurities, since putrefaction soon begins, especially if the temperature is elevated, and hide substance is destroyed, going into solution. It is also indispensable to frequently renew the water in order to retard the growth of bacteria.

With salted hides a much longer soaking is required in order to soften them; it is likewise important to renew the water, that it may more rapidly take up salt and also to keep down destructive bacteria.

Finally with dried hides a still longer soaking is necessary and the renewal of the water is of increased importance; stale water dissolves much hide and occasions a defective grain. There are many tanners of the ancient school who carefully preserve the old liquors from the soaks with the mistaken idea that these soften hides more rapidly than pure water. This is merely apparent and the suppleness acquired by the skin is largely due to loss of its substance by solution.

To sum up, if the tanner wishes good rendement, firm and smooth leather, the soaking should be carried out as rapidly as possible, with renewed water, especially when warm. Any violent motion which may raise the surface of the hide, especially in the case of small skins, should be strictly avoided.

Some tanners think that if a little of the substance of the hide be lost, it is replaced by tannin, and the rendement is not lowered. This is a great error; the amount of tannin absorbed is proportional to the hide substance actually present. There is therefore a double loss affecting the weight of the leather, that of the lost hide and that of the tannin it might have fixed. Research and practical experience have shown that in completed leather there are approximately equal weights of dry hide and dry (combined) tannin. It may be said that a greater quantity of tans than this can be absorbed, but washing extracts this excess which is merely a fraudulent weighting as reprehensible as loading with glucose, lead salts, etc.

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## PATENTS.

**Treatment of Hides, U. S. Patent No. 894,171.** To R. WITHEY, South Bermondsey, England. A process for the treatment of hides consisting in soaking the raw hide taken from the animal in water for a suitable period, about four to seven days for example; then fleshing, liming and dehairing; then steeping it in a mixture of alum and albumen for a suitable period, four to ten days for example; then placing it successively in a series of chemical soaks or baths of graduated strengths each soak consisting of a compound of sulphuric acid, red arsenic and sumac liquor for a suitable period, two days for example, and changing said soaks at suitable intervals, every twelve hours for example; then placing the hide in or treating it with a soak or bath of a solution of rubber, petroleum benzine and naphtha for a suitable period, about two days for example; then air drying, staking, and finishing. The product is to be used for making pneumatic tires.

**Tannin Extract and Process of Producing Same, U. S. Patent No. 894,277.** To F. J. MAYWALD, New York. A process of preparing a dry, friable, soluble tannin extract, substantially non-hygroscopic, by mixing a colloidal carbohydrate such as dextrine with the tannin extract, and then evaporating the mixture to dryness. Fifteen pounds of dextrine are added to 100 lbs. of 51° Tw. extract, the mixture stirred and then evaporated to dryness. Gums like gum arabic, tragacanth, etc., may be substituted for dextrine, and the colloidal material may also be added during the leaching of the bark or wood.

**Composition for Making Artificial Leather, U. S. Patent No. 894,334.** To H. LEWIS, Fitzroy, near Melbourne, Victoria, Australia. A composition of matter consisting of disintegrated leather about 9 lbs., rubber about 4 lbs. petrolatum about 4 ozs., zinc oxid about 12 ozs., pitch about 4 ozs., sulfur, precipitated sulfur, or plumbic oxid about 12 ozs., yellow ocher about 2 ozs., fiber about 2 lbs., antimony about 9 ozs., and vermilion about 2 ozs., compounded together and dipped, sprayed or otherwise permeated with bisulfid of carbon and chlorid of sulfur.

**Process for Making Artificial Leather, Fr. Patent No. 383,612.** To H. LEWIS. (Same as preceding.)

**Evaporator, U. S. Patent No. 894,407.** To T. SUZUKI, Sunamura, Japan. An improved evaporating pan.

**Leather Buffing Machine, U. S. Patent No. 894,502.** To H. A. HOLDER, Lynn, Mass. An improved buffing or whitening machine.

**Leach Clearing Device, U. S. Patent No. 894,618.** To W. FERGUSON, Brevard, N. C. An automatic leach pitcher of the prevailing type.

**Leather Working Machine, U. S. Patent No. 894,839.** To I. G. LEVIN, Chicago, Ill. A glazing or ironing jack of a new type. The irons or glasses are located on the circumference of a rotatable wheel, the leather being supported on a curved support, corresponding to the circumference of the wheel, and adjustable to light or heavy action of the irons, which may be heated while the wheel is rotating.

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Journal of the

# American Leather Chemists Association

Vol. III OCTOBER, 1908 No. 10

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## THE EXTRACTION OF SUMAC AND MYRABOLAMS.[1]

*By Chas. Eachus.*

In a previous report of this committee, results were shown by various methods, and it was deemed advisable to send out additional samples. One sample each of ground sumac and myrabolams were sent to members of the committee. The sumac was pure ground Sicily sumac of good quality and the myrabo-

[1] Final Report of the 1908 Committee.

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lams were of the [J1] variety. The myrabolams were ground fine enough for analysis before sending out, so that any difference in preparation of the sample would not influence results. The following directions were sent to the members of the committee:

I am sending you by express to-day one sample of sumac and one sample of myrabolams for the final work of the committee on the extraction of sumac and myrabolams, of which you are a member. Do not grind the samples, but simply take all of the sample out of each bottle and mix it thoroughly. Then dry from 50 to 100 grams of each sample for not less than three hours at a temperature between 90°-100°C. The loss in weight will give you the percentage of moisture and the sample will be near enough to absolute dryness for practical purposes. From this dry sample, weigh 20 grams for the extraction and extract by the following two methods.

*Method No. 1.* Put 20 grams of dried material in a Teas or Reed extractor cover it with water, and allow it to soak one hour. Then extract by collecting 2000 cc. of the extractive solution outside through lower tube in from six to eight hours.

*Method No. 2.* Put 20 grams of dried material in a Teas, or Reed extractor, cover it with water, and allow it to soak one hour. Then extract by collecting 1500 cc. of the extractive solution outside through lower tube in about four hours, and run reflux with the remaining 500 cc. for four, or six hours longer, so that the extraction can be completed in one day.

Let the extractive solution stand over night and analyze the next day by the official method for extracts, using 50 grams wet hide powder, containing 75% moisture. Use a layer of cotton on the bottom of the extractor to prevent fine material passing through.

The chairman has found that drying the sample absolutely dry before analyzing does not destroy any tannin, but it facilitates the analysis and calculation. If you doubt this it would be well for you to extract 20 grams of the undried material by one, or both methods and report results, which will be appreciated.

If you think the present official method is best, please report results by it also.

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The following results were obtained:

SUMAC.—Method I.

20 gr. extracted with 2000 cc. water, outside entirely.

| Analyst | Total solids | Soluble solids | Insoluble | Non-tannin | Tannin on dry basis | Tannin on air dry basis | Hours extracted outside | Presence of tannin in extracted material | Moisture in sample |
|---|---|---|---|---|---|---|---|---|---|
| Fox... | 53.60 | 51.20 | 2.40 | 18.84 | 32.36 | 29.24 | 6 | slight | 9.65 |
| Russel | 53.71 | 50.23 | 3.48 | 18.59 | 31.64 | 28.67 | 7 | slight | 9.40 |
| Mosser | 53.60 | 51.05 | 2.55 | 19.75 | 31.30 | 28.17 | 7 | | 10.00 |
| Wilson | 54.01 | 51.06 | 2.95 | 19.08 | 31.98 | 29.02 | 7 | strong | 9.25 |
| White. | 54.43 | 51.21 | 3.22 | 19.34 | 31.87 | 29.07 | 6 | none | 8.80 |
| Eachus | 54.26 | 51.96 | 2.30 | 20.08 | 31.88 | 28.85 | 7 | slight | 9.50 |
| Average | | | | | | 29.00 | | | |

SUMAC.—Method II.

20 gr. extracted with 2000 cc. water, 4 hours outside and 4 hours reflux.

| Analyst | Total solids | Soluble solids | Insoluble | Non-tannin | Tannin on dry basis | Tannin on air dry basis | Hours extracted outside | Hours extracted continuous | Presence of tannin in extracted material | Moisture in sample |
|---|---|---|---|---|---|---|---|---|---|---|
| Fox... | 57.00 | 53.85 | 3.15 | 19.66 | 34.19 | 30.89 | 5 | 3 | slight | 9.65 |
| Russel | 57.34 | 53.86 | 3.48 | 19.67 | 34.19 | 30.98 | 4 | 3 | none | 9.40 |
| Mosser | 56.00 | 53.10 | 2.90 | 20.06 | 33.04 | 29.74 | 4 | 4 | | 10.00 |
| Wilson | 56.32 | 53.06 | 3.26 | 19.78 | 33.28 | 30.20 | 4 | 4 | fair test | 9.25 |
| White. | 55.64 | 52.96 | 2.68 | 20.20 | 32.76 | 29.88 | 4 | 4 | none | 8.80 |
| Eachus | 56.94 | 54.42 | 2.52 | 20.73 | 33.69 | 30.49 | 4 | 4 | none | 9.50 |
| Average | | | | | | 30.36 | | | | |

MYRABOLAMS.—Method I.

20 gr. extracted with 2000 cc. water, outside entirely.

| Analyst | Total solids | Soluble solids | Insoluble | Non-tannin | Tannin on dry basis | Tannin on air dry basis | Hours extracted outside | Presence of tannin in extracted material | Moisture in sample |
|---|---|---|---|---|---|---|---|---|---|
| Fox... | 55.20 | 54.30 | .90 | 15.11 | 39.19 | 35.35 | 6 | none | 9.81 |
| Russel | 58.77 | 54.76 | 4.01 | 16.14 | 38.62 | 34.64 | 7 | slight | 10.30 |
| Mosser | 54.65 | 51.42 | 3.23 | 15.69 | 35.73 | 32.16 | 7 | | 10.00 |
| Wilson | 57.26 | 54.59 | 2.67 | 16.28 | 38.31 | 34.39 | 7 | none | 10.22 |
| White. | 55.09 | 53.86 | 1.23 | 15.73 | 38.13 | 34.62 | 6 | none | 9.20 |
| Eachus | 57.52 | 54.96 | 2.56 | 15.89 | 39.07 | 34.85 | 7 | none | 10.80 |
| Average | | | | | | 34.17 | | | |

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MYRABOLAMS.—Method II.
20 gr. extracted with 2000 cc. water, 4 hours outside and 4 hours reflux.

| Analyst | Total solids | Soluble solids | Insoluble | Non-tannin | Tannin on dry basis | Tannin on air dry basis | Hours extracted outside | Hours extracted continuous | Presence of tannin in extracted materials | Moisture in sample |
|---|---|---|---|---|---|---|---|---|---|---|
| Fox... | 57.83 | 55.35 | 2.48 | 15.83 | 39.52 | 35.64 | 4½ | 3½ | none | 9.81 |
| Russel | 58.26 | 55.16 | 3.10 | 16.33 | 38.83 | 34.83 | 4 | 3 | none | 10.30 |
| Mosser | 57.52 | 55.20 | 2.32 | 16.63 | 38.57 | 33.71 | 4 | 4 | | 10.00 |
| Wilson | 58.20 | 55.03 | 3.17 | 16.62 | 38.41 | 34.48 | 4 | 4 | none | 10.22 |
| White. | 56.54 | 54.43 | 2.11 | 15.77 | 38.66 | 35.10 | 4 | 4 | none | 9.20 |
| Eachus | 60.61 | 56.90 | 3.71 | 17.83 | 39.07 | 34.85 | 4 | 4 | none | 10.80 |
| Average..... | | | | | | 34.77 | | | | |

The results of the different members of the committee agree very closely for this sort of work and it shows that these methods will give concordant results, when closely followed on the same sample. The principal point in drawing up a method for the extraction of these materials is to get a uniform method of extraction. The present official method for the extraction of tanning materials is poorly worded and not specific.

*Method No. 1*, which consists of extracting outside entirely is very good from the fact that it gives almost the maximum amount of extractible matter, without running reflux and it is easily carried out.

*Method No. 2*, should be a good modification of the present official method. Its chief advantage is that it will extract all the material that is absorbed by hide powder in eight hours, or less. Most chemists cannot run their extractors over night, and therefore to follow the official method, they must extract two days, allowing the extractor to cool down over night. This is a very poor process and makes the analysis of most materials worthless.

With the sample of myrabolams, these two methods give close results, but in the case of the sumac, there is a difference of over a per cent. tannin between the two methods and naturally the method No. 2 gives the highest results. Most of the members of the committee favor a method of extraction similar to method No. 2, or some such modification of the present official method for crude materials. With all materials, other than sumac, such a method of extraction will not make any difference in the trade,

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but with sumac, it will entirely change the basis of selling sumac. It will raise the percentage of tannin in all sumac in this country 3%, or 4%, and results by American and European chemists will vary more than ever. The Chairman would advise the use of the Procter percolator for sumac extraction, for a few years to come, or perhaps a method of percolation similar to method No. 1 could be used as a compromise. This matter should be decided at the annual meeting this year.

Great care should be paid to the sampling of sumac, and myrabolams, on account of the variation in different bags of the same shipment. The sample should be sent to the chemist in a sealed preserving jar, so that it will not lose moisture. Sumac, when sent in an envelope, will often lose three per cent. moisture, before it reaches the chemist. In grinding myrabolams, care should be taken to get a complete mixture of the hulls and kernels, on account of the difference in tannin in each. The purity of sumac can be determined by means of the microscope and will have to be left to the skill of the chemist.

The Chairman feels that all other points in regard to the choice of a method for these materials can best be discussed at the annual meeting.

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## THE ANALYSIS OF FATS AND OILS.[1]

*By F. W. Alden.*

The experimental work of the committee has been confined to only a few of the more important tests described in the first part of this report (JOURNAL, 1908, 230). It so happened that no one had sufficient time to go through all the work outlined, and such reports as have been received are therefore submitted. It is the opinion of the Chairman that in reporting for the trade the results, with the exception of water, should be calculated to the moisture free basis. The following are not so reported, however, since the figures are only a matter of comparison, and it would seem to simplify matters in this case to base all calculations on the original weight.

[1] **Final Report of the 1908 Committee.**

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*Moisture.*

Both methods were tried with the following results:

| | Oil 1 | | Oil 2 | |
|---|---|---|---|---|
| | Procedure I | Procedure II | Procedure I | Procedure II |
| Russel..... | 28.71 | 28.29 | 22.05 | 21.88 |
| Stillwell (a) ... | 28.90[1] | 28.16 | 22.52[1] | 21.70 |
| (b) ... | 29.06[1] | 28.14 | 22.52[1] | 21.70 |
| Alden ..... | ..... | 28.29 | 22.39 | 21.52 |

[1] Modified.

As far as the above results go they seem to indicate that the method of drying with sand in an oven gives the more concordant results. The Chairman was unable to obtain the moisture on oil 1 by this method on account of spirting. Although he has made hundreds of determinations by this method he has found very few oils that by proper care could not be tested in this way. Serious difficulty is some times experienced, however, which is a drawback to the method. That the figures by the sand oven method show in each case a lower per cent., is a point in its favor, as other substances besides water are undoubtedly driven off. Mr. Russell makes the following comment on this method.

"Of the methods of drying, the one with sand in the oven seems the most satisfactory as it eliminates the error of personal equation which affects results by the method of heating in the platinum dish."

Mr. Stillwell recommends a modified form of the first method, using a test tube 6 inches long and one inch wide instead of a platinum crucible. A test for moisture is made by holding a cold glass rod in the upper part of the tube where it will condense on the rod if not all driven off from the oil.

*Total Unsaponifiable Matter.*

The results by the two methods are as follows:

| | Oil 1 | | Oil 2 | |
|---|---|---|---|---|
| | Procedure I | Procedure II | Procedure I | Procedure II |
| Russel..... | 1.05 | .52 | 20.35 | 17.17 |
| Stillwell (a) ... | 1.64[1] | 1.64 | 19.86[1] | 19.60 |
| (b) ... | 1.64[1] | 1.64 | 19.75[1] | 19.70 |
| Alden ..... | 1.49 | .58 | 21.35 | .... |

[1] Modified, but residue dried for 4 hours.

The Chairman does not report his results for oil 2 procedure II for the reason that he fears there was some loss of

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unsaponifiable during extraction and there was not sufficient time to make a duplicate determination.

Mr. Stillwell offers a modified method in place of Procedure I which he describes as follows:

"In saponifying I use a very strong Alcoholic Potash solution containing no added water. The potash being dissolved in the alcohol direct. Boiling under condenser is kept up for one hour. An equal amount of water is added to the flask, cooled, and poured into a separatory funnel and 50 cc. Petroleum Ether added, and shaken. If it emulsifies, add a little alcohol and agitate gently, when ether solution and soap solution will separate. The soap solution is drawn off into a second funnel, and ether solution washed 3 times with half and half water and 95% alcohol (no trouble is encountered here in getting perfect separation). The soap solution is shaken out a second time with 50 cc. Sulphuric Ether. This ether solution is washed as before and added to main ether solution and whole evaporated and finally dried in water oven. After half hour, if any drops of water show, a little 95% alcohol is added and evaporation, or rather drying, continued for another half hour. This will be the total unsaponifiable matter. If a mineral oil is present, longer drying is absolutely fatal to accurate results, as all mineral oils will slowly volatilize at 212 F.

"It is the writer's opinion that by using this strong alcoholic solution of potash, no trouble will be encountered in saponifying all the higher alcohols, and correct results obtained."

Mr. Russell thinks that his low results on oil 2 by Procedure II may have been due to incomplete extraction, possibly through caking of the material. The Chairman has observed, however, in working with a sample of wool fat, that this method carried the saponification further with a consequent decrease in the unsaponifiables.

### *Total Oxidized Fatty Acids.*

### (*Degras Former*)

Only two reports on this determination are available, which are herewith submitted without comment.

| | Oil 1 | Oil 2 |
|---|---|---|
| Russel | 14.51 | 9.39 |
| Alden | 14.35 | 8.76 |

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*Total Unoxidized Fatty Matter.*
*(Fatty Acids and Unsaponifiables).*

Here, too, only two reports are available, which are also submitted without comment.

| | Oil 1 | Oil 2 |
|---|---|---|
| Russel | 51.58 | 65.13 |
| Alden | 51.51 | 66.59 |

## THE DETERMINATION OF ACIDS USED IN THE TANNERY.[1]

*By J. W. Phelan.*

The committee appointed this year by the council to report on methods for testing tannery acids, consisted of Messrs. A. L. Dean, Allen Rogers, A. D. Little, A. A. Claflin, E. D. Westenfelder, M. F. Nichols, H. R. Browne, A. K. Kilp and L. E. Levi with the writer as chairman.

Believing that more data, such as had been reported (1907) would be of most value, portions of a standard sample of commercial sulphuric, oxalic, formic, acetic and lactic acids were sent to the members of the committee. Instructions as to methods of analysis accompanied the samples. These are the same as given in the report for 1907. Samples were sent the first of February and results were asked for during March.

Mr. A. L. Dean who is associated with A. D. Little reported promptly, as did Mr. F. T. Moses, who is chemist for Mr. A. A. Claflin. These, together with the figures of the chairman, are all the results at hand; although repeated requests, up to a short time ago, have been made of the other members. Mr. B. D. Westenfelder wrote expressing a wish to collaborate but had no laboratory.

Sulphuric acid was analyzed by making an approximately N/5 solution from a known weight of the acid and determining the actual acid content by titration with N/5 alkali and methyl orange. Another method was to evaporate some of the acid with pure ammonia and dry and weigh the residual ammonium sulphate. If this residue be heated and the ammonium sulphate be driven off, the non-volatile impurities may be estimated in the residue.

[1] Report of the 1908 Committee.

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Oxalic acid was titrated directly with standard alkali and phenolphthalein. A check was used in the well-known method of titration with standard permanganate. As commonly practiced, an approximately N/10 solution of potassium permanganate is accurately standardized against a sample of oxalic acid of known purity. To 50 cc. of a solution of the acid to be tested made up of approximately N/10 strength, is added 50 cc. of dilute sulphuric acid (1:10) and the mixture is then heated to about 60°C. It is titrated with the standard permanganate.

Acetic acid was determined by direct titration with standard alkali, using phenolphthalein. Mineral acids were determined by Teas' method in the 1907 report.

Formic acid was titrated with standard alkali and phenolphthalein. No results were reported of a determination of this acid by oxidation, although a method was given.

The total acidity of lactic acid was determined by titrating cold, 5 grams of the commercial acid, as rapidly as possible, with N/2 NaOH, using phenolphthalein as indicator.

The volatile acids were determined by the method of repeated distillation as given by Mr. Claflin in the 1907 report. His method for the anhydrides was also used.

A conclusion with so few results hardly seems possible. However there is no doubt that more data would be highly interesting. Perhaps more explicit directions with methods of standardizing the normal solution would give closer results. The method for volatile acids in commercial lactic acid is still open to improvement, and it is surprising that better results were not obtained on the anhydrides.

| Acids | Phelan | Claflin | Little |
|---|---|---|---|
| | Per cent. | Per cent. | Per cent. |
| Sulphuric... | 91.61 (Tit.) | 92.47 (Tit.)<br>92.58 ($(NH_4)_2SO_4$)<br>.27 (Non-vol.) | 91.51 (Tit.) |
| Oxalic..... | 97.70 ($KMnO_4$) | 99.93 (Tit.)<br>97.25 ($KMnO_4$)<br>.37 ($K_2O$) | 98.45 ($KMnO_4$) |
| Acetic..... | 26.17 | 26.29 | 25.96<br>.10 (Mineral acid) |
| Formic..... | 82.31 | 83.81 | 82.75 |
| Lactic..... | 22.33 | 22.59 | 22.35 |
| Anhydride | 1.26 | 6.51 | 4.86 |
| Volatile... | .918 | .49 | 2.40<br>.15 (CaO) |

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## CURRENT ARTICLES.

*Shoe and Leather Reporter.*

NOTES ON THE MANUFACTURE AND APPLICATION OF FAT-LIQUORS. Aug. 20.

THE TESTING OF RAW MATERIALS. Aug. 20.

TANNERY NOTES. Aug. 20, Aug. 27, Sept. 3, Sept. 10.

CHROME GUSSET SPLITS. Aug. 27.

MEASUREMENT OF LEATHER. Sept. 3.

CHROME TANNED WOOLSKINS AND SHEARLINGS. Sept. 10.

*Hide and Leather.*

DRUM TANNAGE. Aug. 15.

LIMING. Sept. 5.

*Collegium.*

REPORT OF SPECIAL MEETING OF BRITISH SECTION I. A. L. T. C. Aug. 1.

THE DETERMINATION OF THE SOLUBILITIES OF TANNING EXTRACTS. *Dr. J. Paessler* and *T. Veit.* Aug. 15, 22, 29.

PROGRAM FOR THE BRUSSELS CONFERENCE OF THE I. A. L. T. C. Aug. 22 and 29.

*Der Gerber.*

A PECULIAR OCCURRENCE IN PINE LIQUORS. *Dr. W. Eitner,* (concluded) Aug. 1 and 15.

A TANSTUFF REACTION AND ITS APPLICATIONS. E. Stiasny, (Current) Aug. 15

SHOE AND LEATHER EXHIBIT IN VIENNA. Aug. 15.

*Gerber Zeitung.*

THE EMPLOYMENT OF ZEISS' IMMERSION REFRACTOMETER FOR TANNIN ANALYSIS. *K. G. Zwick,* (Concluded) July 16, 17 and 21.

VANADINE BLACK. July 25.

CHROME TANNED SPLITS. July 31.

*Chemiker Zeitung.*

IS THE ASSUMPTION OF CHEMICAL ACTION NECESSARY TO EXPLAIN THE TANNING PROCESS? *E. Stiasny.* No. 50.

*Leather Trades Review.*

THE OFFICIAL CONTROL OF ANTHRAX. *Editorial.* Aug. 12.

DRESSING AND DYEING SHEEPSKIN RUGS. *"Lincoln."* Aug. 12.

THE VOGUE OF THE PIG SKIN. Aug. 12.

THE SUMAC MARKET. Aug. 19.

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*The Leather Manufacturer.*

CHROME TANNED LACE LEATHER. August.

STAINING AND BLACKING CHROME LEATHER. August.

BEAMHOUSE PROCESS FOR CALFSKINS. August.

FLOOR PLAN OF SMALL SOLE LEATHER TANNERY. August.

HEATING SYSTEMS FOR MILLS. *A. J. Hosmer.* (Current), August.

OLD AND NEW TANNING METHODS. *C. A. Brown.* August.

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## REVIEWS.

**The Two Methods of Tannin Analysis.** J. PAESSLER. *Gerber Zeitung*, 1908 [51], No. 103.—In this report to the Central Union of German Leather Industries, the author gives his reasons for opposing the adoption of the new method of analysis. Those who favor the shake method claim that its results are more in accordance with practice in the works; this is a conjecture and difficult to prove. The methods in tanning are so varied that in one case the figures obtained by the filter method may apply, in another, those by the shake method. The results of analysis then can merely show relative amounts of tan-stuffs in different materials and in ascertaining this, the new method offers no advantage, as evidenced by the numerous publications of discrepant results. The new method needs more precise definition before displacing the old.

**The Two Methods of Tannin Analysis.** F. ROSER. *Gerber Zeitung*, 1908 [51], No. 103.—In this report, the opposite view is taken to that above. When a new method of analysis is introduced, it will for a time naturally cause some friction and differences in results. The new method according to the opinion of the author determines tan-stuffs more sharply and does not bring in non-tans as "tanning substances." An example from the laboratory of Dörr and Reinhart speaks for itself. A liquor containing vegetable dyes was analyzed; by the new method the filtrate was strongly colored, only tans had been absorbed; with the filter method, the filtrate was colorless, dyes and tans together were reckoned as "tanning substances." For the same reason a quebracho extract blended with myrabolams and containing more non-tans, will give greater differences by the two methods than pure extract.

**Meeting of the German Section of the International Association.** *Collegium*, 1908, No. 316, pp. 243-50.—The meeting was held at Frankfurt a. M., May 31, Dr. Becker presiding. Dr. Paessler presented the Report of the Commission on Tannin Analysis. In the discussion of the results Dr. Becker attributes the discrepancies to the Freiberg hide powder, which contains 10% solubles, the American being much better. Dr. Sichling in support of his alterations of procedure with the shake method claims the loss of washing hide powder to be too great and too variable; the silver chromate test he finds unsatisfactory; the increase of solubility on storage of

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moist hide powder is slight. Dr. Wegner thought 7-8 washings necessary; moist powder keeps unaltered several days in a chloroform atmosphere. Dr. Voiges disputes the possibility of detecting adulteration of quebracho extract by differences in results obtained by the two methods as stated by Schorlemmer and Sichling. (This JOURNAL, 1908, p. 91). It was agreed that the Commission be continued.

Herr Kallat-Offenbach spoke upon physical color analysis and described his own patented apparatus.

Dr. Paessler described his process or the determination of sulphur in leather according to the method of Brunk used for coal; igniting with soda and cobalt oxide in a current of oxygen. Schopper's electric ignition apparatus is used, heating 20 minutes.

**Report of the German Section's Commission on Tanning Analysis.** J. PAESSLER. *Collegium*, 1908, Nos. 315, 316, pp. 209-42.—The report opens with an account of some preliminary experiments made at the Frieberg Station.

I. *Comparison of Ready and Fresh Chromed Hide Powder.*—The non-tans in six extracts were determined to test the reliability of the weak chromed hide powder furnished by the Station.

| | Filter method | Shake method: Ready chromed | Shake method: Fresh chromed |
|---|---|---|---|
| R. I | 3.4 | 5.7 | 5.8 |
| R. III | 3.7 | 5.0 | 5.0 |
| R. V | 3.1 | 4.9 | 4.9 |
| G. II | 2.5 | 5.1 | 5.1 |
| G. III | 3.4 | 5.3 | 5.0 |
| G. IV | 2.8 | 5.7 | 5.2 |

Ready chromed powder therefore gives the same results and its use is recommended as simplifying the work.

II. *Influence of Age Upon Ready Chromed Hide Powder.*—Protracted storage does not affect the absorbing power of the weak chromed hide powder as shown in the table:

| | Weak chromed powder | | | | | | | Fresh chromed | |
|---|---|---|---|---|---|---|---|---|---|
| Method | F. | S. | F. | S. | F. | S. | F. | S. | Shake |
| Quebracho extr | 1.9 | 3.7 | 2.2 | 3.8 | 3.1 | 4.2 | 2.8 | 3.9 | 4.0 |
| Chestnut extr | 12 9 | 14.9 | 13.0 | 15.1 | 12.7 | 15.8 | 13.1 | 15.2 | 14.8 |

III. *Influence of Chromium Content.*—According to the International Commission, the percentage of $Cr_2O_3$ should be within the limits 0.5-2.0. Two quebracho extracts gave:

| | Filter method: Ready chromed | Shake method: Ready chromed | Shake method: Fresh chromed with chloride solution of 2% | 4% | 8% |
|---|---|---|---|---|---|
| $Cr_2O_3$ in powder of 16% $H_2O$ | 0.5 | 0.5 | 0.6 | 0.9 | 1.4 |
| Non-tans, Extr. No. 1 | 3.5 | 5.5 | 5.3 | 5.0 | 6.2 |
| " " " " 2 | 3.0 | 5.0 | 5.2 | 5.6 | 6.4 |

Although still within the limits, the results are higher with increased

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chromium. It is recommended that the chroming be made with 2% chromium chloride.

IV. *Influence of Chromium Content in Ready Chromed Hide Powder.*—Experiments are cited showing that this is of little influence and stronger chroming than previously used is not recommended.

V. *Influence of Time of Shaking.*—Three forms of apparatus were compared differing in speed. It was found that the results were the same within periods of 5 to 20 minutes.

VI. *Influence of Sugars and Bisulphites.*—Some hold that these substances are in part reckoned as tans. Experiments upon known mixtures made from pure quebracho extract showed that by neither the filter or shake method was sugar or bisulphite taken up by the hide powder, but rather that their presence slightly lowered the absorption of tan-stuffs.

VII-XI. *Comparative Analyses of Tan Extracts.*—These were made by the Commission, the members being here designated in the tables by letters; (B) Dr. Bosh, (M) Dr. Moll, (P) Prof. Dr. Philip, (S) Dr. Sichling, the Freiberg Station being represented by (Sdl.) Herr Seidel and (V) Herr Veit.

It has been found somewhat difficult to press washed hide powder down to a content of 20 grms. of water. To get over this, less pressure can be used and the liquid made up to 150 instead of 120 cc.; determinations are included according to this process. Besides the filter and shake methods a combination of both was used, here designated as Veit's method. The process is as follows: 7 grms. hide powder are placed in a filter bell and 30 cc. drawn off from the original solution of 125 cc. The hide powder is then separated and shaken with the remaining liquid in the usual way. This method on account of its simplicity is recommended for trial and possible improvement. Analyses involving the addition of kaolin to the de-tanned solutions are included; this is however considered necessary as a clear solution may be obtained by repeated filtration. Moreover in some cases an absorption of non-tans by kaolin was observed.

*VII. Quebracho Ext. (liquid).*

| | B. | M. | P. | S. | Sdl. | V. |
|---|---|---|---|---|---|---|
| Total soluble | 39.1 | 37.0 | 39.1 | 38.6 | 37.5 | 38.3 |
| Non-soluble | ... | 3.0 | 0.9 | 1.3 | 2.5 | 2.0 |
| Non-tans | | | | | | |
| Filter method | 4.9 | 3.8 | 3.7 | 4.5 | 4.45 | 4.75 |
| Veit's method | 6.1 | 4.25 | 5.1 | 4.5 | 5.0 | 5.05 |
| Shake method: | | | | | | |
| 150 cc., ready chromed | ... | ... | ... | ... | 5.9 | 6.3 |
| Same, with Kaolin | ... | ... | ... | ... | 5.7 | 5.7 |
| 120 cc., ready chromed | 6.3 | 4.25 | 4.9 | ... | 5.75 | 5.8 |
| 150 " fresh " | ... | ... | ... | ... | 5.2 | 4.85 |
| 120 " " " | 5.4 | 3.8 | 5.1 | 6.2 | 4.9 | 5.2 |

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*VIII. Quebracho Ext. (solid).*

| | B. | M. | P. | S. | Sdl. | V. |
|---|---|---|---|---|---|---|
| Total soluble | 78.85 | 78.8 | 80.5 | 78.7 | 79.7 | 79.8 |
| Non-soluble | ... | 8.3 | 7.2 | 8.5 | 8.1 | 7.7 |
| Non-tans | | | | | | |
| Filter method | 5.95 | 5.35 | 5.85 | 5.7 | 6.45 | 6.3 |
| Veit's method | 6.75 | 6.95 | 7.5 | 7.3 | 7.85 | 7.65 |
| Shake method : | | | | | | |
| 150 cc., ready chromed | ... | ... | ... | ... | 9.3 | 10.2 |
| Same, with Kaolin | ... | ... | ... | ... | 9.7 | 10.4 |
| 120 cc., ready chromed | 8.85 | 6.7 | 7.0 | 11.9 | 8.95 | 9.45 |
| 150 " fresh " | ... | ... | ... | ... | 9.65 | 9.7 |
| 120 " " " | 7.35 | 6.9 | 7.6 | 9.6 | 9.6 | 9.45 |

*IX. Quebracho Ext. (sulphited).*

| | | | | | | |
|---|---|---|---|---|---|---|
| Total soluble | 41.95 | 41.95 | 42.3 | 42.3 | 41.9 | 42.4 |
| Non-soluble | ... | 0.45 | 0.3 | 0.0 | 0.6 | 0.1 |
| Non-tans | | | | | | |
| Filter method | 9.35 | 7.9 | 9.5 | 8.5 | 8.4 | 8.4 |
| Veit's method | 9.15 | 9.2 | 10.3 | 10.0 | 9.6 | 10.3 |
| Shake method : | | | | | | |
| 150 cc., ready chromed | ... | ... | ... | ... | 10.7 | 11.55 |
| Same, with Kaolin | ... | ... | ... | ... | 10.4 | 11.3 |
| 120 cc., ready chromed | 9.5 | 8.9 | 10.4 | 10.8 | 10.65 | 10.35 |
| 150 " fresh " | ... | ... | ... | ... | 10.35 | 10.2 |
| 120 " " " | 9.55 | 9.1 | 10.5 | 11.5 | 10.2 | 10.1 |

*X. Chestnut Ext.*

| | | | | | | |
|---|---|---|---|---|---|---|
| Total soluble | 40.45 | 40.35 | 40.1 | 40.6 | 40.1 | 40.7 |
| Non-soluble | ... | 0.5 | 0.45 | 0.3 | 0.9 | 0.3 |
| Non-tans | | | | | | |
| Filter method | 11.0 | 10.7 | 11.05 | 11.6 | 11.25 | 11.55 |
| Veit's method | 12.85 | 12.9 | 14.2 | 13.2 | 12.95 | 14.0 |
| Shake method : | | | | | | |
| 150 cc., ready chromed | ... | ... | ... | ... | 13.6 | 14.5 |
| Same, with Kaolin | ... | ... | ... | ... | 13.3 | 14.4 |
| 120 cc., ready chromed | 13.7 | 12.7 | 14.55 | 14.0 | 13.9 | 13.55 |
| 150 " fresh " | ... | ... | ... | ... | 13.7 | 14.5 |
| 120 " " " | 14.25 | 12.05 | 13.8 | 14.0 | 13.9 | 12.9 |

*XI. Oak Wood Ext.*

| | | | | | | |
|---|---|---|---|---|---|---|
| Total soluble | 41.0 | 40.85 | 41.3 | 41.3 | 40.4 | 39.5 |
| Non-soluble | ... | 0.6 | 0.3 | 0.2 | 1.1 | 1.9 |
| Non-tans | | | | | | |
| Filter method | 12.95 | 12.7 | 13.1 | 13.6 | 13.0 | 13.55 |
| Veit's method | 14.1 | 14.35 | 15.0 | 14.6 | 14.9 | 15.15 |
| Shake method : | | | | | | |
| 150 cc., ready chromed | ... | ... | ... | ... | 15.4 | 15.25 |
| Same, with Kaolin | ... | ... | ... | ... | 15.0 | 15.05 |
| 120 cc., ready chromed | 14.75 | 14.15 | 14.9 | 15.1 | 15.15 | 15.15 |
| 150 " fresh " | ... | ... | ... | ... | 14.35 | 15.15 |
| 120 " " " | 15.3 | 14.1 | 15.1 | 15.6 | 14.3 | 14.3 |

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The variations in determinations of insolubles are attributed to personal equation of the analyst in judging an "analytically clear" solution. The filter method gave 1.1% as the average of the greatest differences in the determination of non-tans, while the shake method gave 2.3%. Dr. Sichling deviated from the official method, preferring not to weigh the moist hide powder but to determine its water directly by drying four hours. Leaving out his results the average difference for the shake method is brought down to 1.85%.

*XII. Condensed Average Results for Non-Tans.*

| Extract Number | VII | VIII | IX | X | XI |
|---|---|---|---|---|---|
| Filter method | 4.4 | 5.9 | 8.7 | 11.2 | 13.2 |
| Veit's method | 5.0 | 7.3 | 9.8 | 13.4 | 14.7 |
| Shake method: | | | | | |
| Ready chromed | 5.4 | 8.8 | 10.1 | 13.7 | 14.9 |
| Fresh chromed | 5.1 | 8.4 | 10.2 | 13.5 | 14.8 |

In agreement with the preliminary experiments (I) the results obtained with ready or fresh chromed powder average nearly equal. Veit's method yields in most cases figures concordant with others by the shake method. From the results in tables VII-XI it is seen that the absorbing power of the hide is slightly lowered on the greater dilution to 150 cc., however the differences are too slight and the analyses too few to draw certain conclusions.

XIII.—A report from Herr Zeuthen, chemist to Dr. Moll of the Commission is included in explanation of the uniformly lower results obtained by the latter. Dr. Sichling's method is criticized as leading to higher results from the moist hide becoming soluble during the delay for the drying determination and experiments are cited in proof. This error more than balances the advantage gained in avoiding washing which Jedlicka has shown to be insignificant. (This JOURNAL, 1908, p. 95). It is recommended to rather use the washed hide immediately after pressing. The washing of fresh chromed hide powder should be continued till giving the silver test; ready chromed powder should be washed at least three times.

XIV. *Degree of Washing.*—Some attribute variations in results by the shake method to insufficient washing and also to protracted washing increasing the solubility of hide substance. Experiments in this direction showed that at least four washings are necessary; qualitative tests should of course be made. Continued washing does not effect the results essentially and does not account for the great variations obtained by different analysts.

XV-XX. *Second Series of Non-Tan Determinations.*—The concordance in results by the shake method obtained in the first series (VII-XI) leaving much to be desired, the Commission made a second series, determining the non-tans only, without use of kaolin, in six extracts. The detailed tables are here omitted, the condensed results following.

The same analysts took part except one; here (A) indicates Dr. Arnoldi for Freiberg.

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| | B. | M. | P. | S. | A. | V. |
|---|---|---|---|---|---|---|
| *XV. Quebracho Ext.* | | | | | | |
| Filter method | 4.85 | 4.9 | 4.1 | 4.9 | 3.75 | 4.7 |
| Veit's method | 4.55 | 4.45 | 4.9 | 4.95 | 4.75 | 5.0 |
| Shake method: | | | | | | |
| 150 cc., ready chromed | 5.1 | 4.55 | 4.2 | 6.15 | 5.9 | 5.55 |
| 120 " " " | 4.8 | 4.45 | 4.2 | 5.5 | 4.7 | 5.45 |
| 150 " fresh " | 4.45 | 4.25 | 5.0 | ... | 4.6 | 5.5 |
| 120 " " " | 4.15 | 4.25 | 4.8 | 5.65 | 4.1 | 4.9 |
| *XVI. Quebracho Ext.* (*sulphited*). | | | | | | |
| Filter method | 8.2 | 9.15 | 9.6 | 9.45 | 9.55 | 9.35 |
| Veit's method | 9.4 | 10.35 | 10.6 | 11.15 | 11.75 | 11.9 |
| Shake method: | | | | | | |
| 150 cc., ready chromed | 10.1 | 10.15 | 10.9 | 13.7 | 11.3 | 11.45 |
| 120 " " " | 9.85 | 10.2 | 10.8 | 12.25 | 10.85 | 11.35 |
| 150 " fresh " | 10.25 | 10.8 | 11.25 | 13.25 | 10.75 | 11.5 |
| 120 " " " | 10.45 | 10.7 | 10.5 | 14.05 | 10.35 | 11.3 |
| *XVII. Quebracho Ext.* (*solid*). | | | | | | |
| Filter method | 18.0 | 18.85 | 17.5 | 18.95 | 20.0 | 18.85 |
| Veit's method | 19.1 | 19.3 | 20.3 | 19.85 | 19.85 | 21.4 |
| Shake method: | | | | | | |
| 150 cc., ready chromed | 19.55 | 19.45 | 20.85 | 24.9 | 21.9 | 21.45 |
| 120 " " " | 18.7 | 19.2 | 20.0 | 22.05 | 20.6 | 21.7 |
| 150 " fresh " | 19.8 | 19.5 | 20.0 | 23.7 | 19.9 | 21.55 |
| 120 " " " | 19.75 | 19.35 | 19.85 | 23.1 | 20.1 | 21.45 |
| *XVIII. Chestnut Ext.* | | | | | | |
| Filter method | 11.75 | 12.3 | 12.4 | 12.55 | 11.95 | 12.2 |
| Veit's method | 13.0 | 13.6 | 14.1 | 13.9 | 15.2 | 14.35 |
| Shake method: | | | | | | |
| 150 cc., ready chromed | 13.25 | 13.75 | 13.95 | 15.1 | 14.1 | 14.35 |
| 120 " " " | 12.7 | 13.6 | 14.0 | 15.25 | 14.1 | 14.7 |
| 150 " fresh " | 13.8 | 13.1 | 14.4 | 14.6 | 13.6 | 13.8 |
| 120 " " " | 13.4 | 13.0 | 14.45 | 14.75 | 13.75 | 13.75 |
| *XIX. Myrabolams Ext.* | | | | | | |
| Filter method | 11.95 | 13.0 | 13.8 | 13.25 | 12.1 | 12.35 |
| Veit's method | 15.4 | 16.3 | 16.1 | 16.75 | 17.9 | 17.3 |
| Shake method: | | | | | | |
| 150 cc., ready chromed | 15.25 | 16.05 | 17.2 | 19.2 | 16.65 | 16.9 |
| 120 " " " | 15.1 | 15.85 | 17.1 | 18.45 | 16.2 | 17.05 |
| 150 " fresh " | 15.4 | 16.7 | 17.1 | ... | 16.2 | 16.95 |
| 120 " " " | 15.2 | 16.65 | 16.6 | 18.3 | 16.45 | 16.65 |
| *XX. Pine Ext.* | | | | | | |
| Filter method | 21.15 | 21.7 | 21.5 | 22.6 | 22.3 | 22.15 |
| Veit's method | 21.75 | 23.65 | 25.2 | 24.05 | 24.65 | 24.1 |
| Shake method: | | | | | | |
| 150 cc., ready chromed | 23.15 | 24.0 | 25.0 | 26.65 | 24.1 | 24.35 |
| 120 " " " | 23.1 | 23.75 | 24.8 | 25.7 | 23.55 | 24.8 |
| 150 " fresh " | 25.65 | 24.2 | 26.1 | 26.15 | 24.1 | 23.8 |
| 120 " " " | 25.55 | 23.95 | 25.4 | 25.75 | 23.9 | 23.6 |

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*XXI. Condensed Table of Maximum Differences in XV-XX.*

| | Extract | Filter method a | Veit's method b | Shake method c | Shake method d | Shake method e | Shake method f |
|---|---|---|---|---|---|---|---|
| XV. | Quebracho, liquid | 1.15 | 0.55 | 1.70 | 1.05 | 1.25 | 0.80 |
| XVI. | " sulfited | 1.40 | 2.50 | 1.35 | 1.50 | 1.25 | 0.95 |
| XVII. | " solid | 2.50 | 2.30 | 2.00 | 3.00 | 2.05 | 2.10 |
| XVIII. | Chestnut | 0.65 | 2.20 | 1.10 | 2.00 | 1.30 | 1.55 |
| XIX. | Myrabolams | 1.85 | 2.50 | 1.95 | 2.00 | 1.70 | 1.45 |
| XX. | Pine | 1.15 | 3.45 | 1.85 | 1.70 | 2.30 | 1.95 |
| | Average | 1.45 | 2.25 | 1.66 | 1.88 | 1.64 | 1.47 |
| | | | | | | 1.66 | |

The four variations of the shake method are (c) ready chromed hide powder, 150 cc. liquid; (d) same, 120 cc.; (e) fresh chromed, 150 cc.; (f) same, 120 cc. The filter method shows the least differences, Veit's method the highest.

*XXII. Condensed Average Values of Non-Tans.*

| Extract Number | XV | XVI | XVII | XVIII | XIX | XX | Average |
|---|---|---|---|---|---|---|---|
| (a) Filter method | 4.5 | 9.2 | 18.6 | 12.2 | 12.7 | 21.9 | 13.2 |
| (b) Veit's method | 4.8 | 10.9 | 20.0 | 14.0 | 16.6 | 23.9 | 15.0 |
| Shake method: | | | | | | | |
| (c) Process | 5.1 | 10.8 | 20.6 | 13.9 | 16.4 | 24.1 | 15.2 |
| (d) Process | 4.8 | 10.6 | 20.0 | 13.9 | 16.3 | 24.0 | 14.9 |
| (e) Process | 4.8 | 10.8 | 20.1 | 13.7 | 16.5 | 24.8 | 15.1 |
| (f) Process | 4.4 | 10.7 | 20.1 | 13.7 | 16.3 | 24.5 | 15.0 |
| Average (c.-f.) | 4.8 | 10.7 | 20.2 | 13.8 | 16.4 | 24.4 | 15.05 |

This shows that in the shake method, it is immaterial whether ready or fresh chromed hide powder be used or the volume of liquid be 120 or 150 cc. The chairman (Dr. Paessler) recommends that ready chromed powder be used, but a volume of 120 cc. in accordance with original directions. Veit's method gives the same average results but greater differences (see XX) than in the first series; perhaps this simpler method may be improved.

XXIII—Experiments were made at the Freiberg Station bearing upon Sichling's process; ready chromed powder was used, and 120 cc. final dilution. The conclusions were that Sichling's method gives somewhat higher non-tans than the official method. By keeping a day's supply of moist hide powder at a low temperature (12°C, in the cellar) in well closed boxes, the results are not affected; at essentially higher temperatures, hide goes into solution. In the test made, the amount of water to be added by Sichling's method was 3.4 cc., by the official method, 6.4 cc.; since the last would give greater dilutions, the non-tan determination would be less. The water determination by Sichling's method is certainly more accurate, since direct, and was found complete in 4 hours.

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That it comes out higher is attributed to loss of hide powder by washing, a trial showing such loss in one case to be 0.34 grms.

In conclusion the shake method offers no superiority in concordance of results. If retained, the details should be more precise and accordingly more experimental data must be collected.

**Report of the Meeting of the Austro-Hungarian Section of the International Association.** E. STIASNY. *Der Gerber*, 1908, [34], No. 812, pp. 175-6.—The President, W. Eitner, spoke upon the superiority of the chromed hide powder methods of analysis which originated in the Vienna Station. While the Americans have adopted the Vienna method with slight alteration, there has been resistance in other quarters, particularly Germany. Notwithstanding the adoption of the shake method as official by the International Association at Frankfurt in 1906, some members of the German Section have ignored the painstaking labors of the Commission on analysis. The extract buyers must be educated to know that a guaranteed certain strength by the new method is equivalent to a higher rating by the old.

A resolution was adopted deprecating the action of those of the German Section adhering to the old method in the interest of certain extract makers.

The papers read will be published in "*Der Gerber.*"

**The Present Situation in the Tannin Analysis Question.** M. SMAIC. *Der Gerber*, 1908, [34], No. 813, 192-3.—Since the Frankfurt Conference the Vienna methods have been gaining ground. In making comparative analyses at that time, the writer found that the results were much the same, whether the hide powder was chromed strong or weak, used wet or dry, shaken or left stand over night. The Vienna Station is now striving to prepare a good dry chromed powder, unalterable on storage. In the comparative analyses with this powder given below, 8-10 grms. dry hide powder were stirred with 30 cc. water after two hours 120 cc. liquor added, left stand over night and 50 cc. evaporated. The result was the same on shaking one-fourth to one-half hour.

| | Non-tans | |
|---|---|---|
| | Quebracho ext. | Oakwood ext. |
| Official method..... | 5.01 | 12.58 |
| Dry hide-powder, 4.28% $Cr_2O_3$ .... | 4.96 | 12.55 |
| Dry hide-powder, 5.98% $Cr_2O_3$ .... | 5.02 | 12.57 |

**A Fault Common to Both Methods of Tannin Analysis.** E. SCHELL. *Collegium*, 1908, No. 319, pp. 272-4.—Judging by the numerous publications on the subject, the new method is just as subject to variations as the old; concordant results may be obtained by the same analyst but discrepancies are frequent in different laboratories. The writer believes that one cause of error, common to both methods is the concentration of solution during protracted filtration, especially in vacuo. A letter from Dr. Paessler (Apr., 1907) is quoted reporting total solubles in a sulphited extract

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filtered by suction; one-half hour gave 45.7%; three hours, 46.4%; five and one-half hours, 47.3%. The writer considers this a weak point in either method, the practice in filtration being so variable and finds it difficult to see the advantage of bringing in a new method having the same defects as the old and some new sources of error of its own.

**Poisoning by Chromium in Industrial Operations.** PROF. LEWIN, from *Chemiker Ztg.* through *Ledermarkt*, 1908, [30], No. 50.—The laws provide to some extent for the protection of workmen engaged in the manufacture of chromium compounds, but it is equally important that precaution should be taken in the industries where these products are employed. All chromium compounds whatever are poisonous, including the basic as well as the acid oxide. Not only may the tissues be affected by direct contact, but as shown by experiment upon living animals and observation of the human being, chromium may be absorbed through the skin and enter the blood, producing disease of the stomach and particularly of the kidneys. In the latter case the urine becomes albuminous and is found to contain chromium. Aside from the self-evident precautions, the restriction of the time spent by the workman in this line is of importance, in order that the system may regularly resist the poison and recover from its attacks. Above all, the workman himself should be posted in this matter and it is proposed that he be furnished with the information.

*Instruction Sheet for Chromium Workman.*—These include those in chemical and match factories, dyers, fullers, tanners, textile printers, painters, etc.

(1) All chromium compounds are poisonous, in mass or powder, mixed with water or in solution. A detailed list of these follows, principally pigments.

(2) Any are liable to chromium poisoning, who handle or inhale these substances. A list of operations is given where this may happen.

(3) The injury may take place in two ways; (1) by direct contact with the skin especially the hand also the inner surface of nose, mouth or throat; (2) by entering the blood.

(4) The action of chromium compounds superficially is described at some length; production of local inflammation, blisters, open sores, secretions and bleeding from the nose, affection of the nostrils culminating in destruction of the partition, etc. When introduced in the blood, headache and pain in the stomach results, and finally kidney disease.

(5) Protection and prevention; direct handling should be avoided when possible, otherwise the hands guarded by gloves or rubbing vegetable oils into the flesh. Eating and drinking on the premises should be avoided. The urine should be periodically examined by a physician.

**Glycerine.** *Gerber Zeitung*, 1908, [51], No. 105.—This is generally obtained from the stearic acid manufacture. Because of its high boiling point (290°C) glycerine remains in leather on drying and gives it a certain flexibility. Nevertheless, its application in tanning is limited, since it absorbs water from the air, and leather strongly impregnated with it

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never thoroughly dries. It cannot be substituted for fat, for it is soluble in water and is easily washed out. It can however be added with advantage up to 10% to soap dressing for dry and slightly greased upper leather. It can also be added to glazes, etc., preventing their becoming brittle. Since it mixes with spirit it may be used in resin or shellac glazes. Glycerine cannot however be regarded as a good dressing material for leather, because of its solubility and over 10% should not be added to a grease or fat liquor. Hard and brittle inner soles are made milder by treatment with glycerine.

**Why Do Many Fail with Shellac Glaze?** *Gerber Zeitung*, 1908, [51], No. 105.—Shellac glaze is superior to all others applied for direct effect, not only in gloss, but in durability, resisting acids and alkalies. Its application however is the most difficult requiring a certain skill. First of all, because of the rapid evaporation of the alcohol, the glaze must be prepared very thin. It cannnot be considered a covering glaze like glue, blood, etc., and requires well-finished leather. Also several applications are necessary, each drying separately. Another cause of failure is due to the solvent action of the alcohol upon the greasy or soiled parts of the grain, causing spots; the leather therefore should contain little fat. The grain should be well cleaned before glazing, best with a barberry solution. The glazing should be applied in short rapid strokes, taking out only enough for one hide at a time; even then a little alcohol should be added from time to time to make up for evaporation.

**Invastin Preparations.** *Gerber Zeitung*, 1908, [51], No. 111.—This new material for leather finishing manufactured by the *Chemische Fabrik Obergruna*, Siebenfehn, Saxony, is intended to take the place of pastes from Irish moss, tragacanth, etc.; unlike these, which form a slime with water, invastin goes completely into solution. It quickly penetrates the leather, giving the other ingredients of the dressing a fine hold upon the fibre which also preserves its natural appearance. It is especially suited for fine vache leather, withstanding beating upon the table. Invastin does not contain sugar or other ingredients commonly rated as intentional weighting ingredients in dressings. A further advantage is superior resistance to moisture.

**How to Soften Hard Vegetable or Chrome Tanned Leather.** *Gerber Zeitung*, 1908, [51], No. 114.—It is well known that any leather on storage becomes stiff and hard under certain conditions; these are frequent changes of temperature and humidity of the surrounding air. This hardening is not considerable with well tanned and properly greased leather; a superficial reworking by stretching or staking makes it again flexible. With poorly tanned or insufficiently greased stock however, the fibres shrink together on moistening and form a hard mass on drying. Mechanical treatment may soften such stock for a time but the fault reappears on storage. The remedy is to completely soak the leather again and treat once more with tanning material or grease, singly or both according to need. Sumac is best suited for after tannage, as it tans soft, penetrates well and affects the original

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color the least. For treating 100 kg. softened chrome leather .6-8 kg. sumac extract are made up with luke-warm water to 100 litres, and in this the leather is wheeled one hour. It is then rinsed, blackened, oiled on the grain with bone-oil and further curried as usual. By another method, the leather is treated direct without soaking for several minutes at 30°R. with a very weak, clear solution of sumac of 1½ to 2°B., the tan immediately penetrating the leather. A second blackening of the leather is also necessary in this process. On account of the difficulty with which once dried chrome leather takes up the black, it is best to apply this (aniline black) well warmed. Vegetable tanned leather that is re-tanned with sumac, is also best greased with thin fat, whale or bone-oil with the difference, especially in the case of heavy leather, that both sides are greased. This process is also used with both sorts of leather when only greasing without retanning is necessary. According to Rieder, the second tanning and greasing can be combined in one operation, employing an emulsion.

For heavy chrome leather, intended for straps, etc., a mixture for re-greasing may be prepared from two parts tallow, one part degras. This is applied lightly on the grain, more thickly on the flesh side and milled in warm for 1½ to 2 hours. The leather is then immediately beaten on the table, degreased, dried, again beaten, and glazed.

**Behavior of Gelatine Solutions with the Naphthols, and their Mixtures with Formaldehyde.** A. WEINSCHENK, from *Chemiker Ztg.*, through *Gerber Zeitung*, 1908, [51], No. 124.—The author refers to his former publications on the tanning of hide by naphthols aided by formaldehyde (*Chemiker Ztg.*, 1907, p. 549; Germ. Pat. 184,449). Stiasny's criticism of this process (this JOURNAL 1907, p. 233) ascribing the tanning agency solely to the formaldehyde is declared untenable and his experiments as not really testing the matter. The author defines the action of β-naphthol upon hide as a marked drawing together of the fibres similar to the action of tan-stuffs. This "adstriction" power is increased considerably by formaldehyde. If powdered α- or β-naphthol be stirred into a luke-warm solution of gelatine, the naphthol readily dissolves although little soluble in pure water; soluble naphthol-gelatine has been formed as proved by diazo compounds, for instance from *p*-nitraniline, forming a soluble red dye; were the naphthol free, an insoluble azo-dye would precipitate. β-naphthol-gelatine is not precipitated by salt solution within wide limits. To prepare this compound, four gms. β-naphthol are dissolved warm in 20 cc. glycerine and 20 gms. gelatine dissolved in a little water added, heating on the water-bath one-quarter hour, finally pouring all into 400 cc. luke-warm water, forming a permanent solution to be filtered in 24 hours, first melting if any gelatinizing has taken place. This gives a solution rich in the naphthol-gelatine compound. If salt be added to such a solution to five per cent. and then formaldehyde, naphthol-formaldehyde-gelatine is precipitated, completely insoluble in water. To show that the naphthol takes part here, the following experiment may be made. To 10 gms. gelatine and 50 gms. salt dissolved in one litre water, formaldehyde solution is added equivalent to one gm. pure aldehyde. Such a solution gelatinizes only at low temper-

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atures and is then readily melted. If this be warmed to 30°C. and five to 10 gms. powdered $\alpha$- or $\beta$-naphthol stirred in, an insoluble compound forms, the precipitation being complete in one-half hour. This shows that the naphthol has tanned the gelatine under conditions where formaldehyde alone was unable to do this.

**The Ammonia Content of Lime Liquors.** VICTOR ARNSTEIN. *Gerber Zeitung*, 1908, [51], No. 134.—In general the amount of $NH_3$ present is proportional to the age of the lime, the capacity for dissolving hide increasing with time. The lime in solution, together with the bacteria of fermentation, dissolve the mucous layer of the hide, forming amino-compounds and finally carbonic acid, water and ammonia, which increase the solvent action of the liquor on the hide. Hence the ammonia content serves to some extent to gauge the composition and character of used lime liquors.

In the following ammonia determinations made at the Freiberg Tanning School, the ammonia was distilled off the liquor at the lowest possible temperature to avoid formation of additional ammonia by overheating during the analysis. Procter and McCandlish have shown this precaution to be necessary. (*Collegium*, 1906, p. 270). A series of three Erlenmeyer flasks of 300 cc. capacity were used; the first contained the liquor for examination heated on the water-bath and the other two a measured amount of $N/10 H_2SO_4$ for absorption of the evolved $NH_3$. The water-bath was kept below 85° C., giving a temperature of 65-70° to the assay liquor. A current of air, freed from $NH_3$ and $CO_2$ was drawn through the flasks during the analysis. Test experiments with known solutions showed that all the ammonia was expelled in one-half hour. A little paraffin oil was added to prevent frothing. A series of preliminary blank tests with known ammonia solutions to which had been added lime-water, sodium sulphide and gelatine, are detailed; each of these additions were shown not to affect the result. The following series of ammonia determinations in used lime liquors were then made (methyl orange indicator). The limes used were for Vache leather, consisting of two vats of 1½ cbm. capacity, used alternately for white and "sharpened" limes. The white lime charge was 20 kg. lime and used as such for 3 to 4 lots of 15 hides each, adding 10 kg. lime with each lot of hides. The hides are brought into the white lime after remaining 3 to 4 days in the "sharpened" lime. After use, the white lime is "sharpened" with 2½ kg. sodium sulphide for each lot of fresh hides.

*Record for One Vat:*

| No. | Date | Mg. $NH_3$ in 100 cc. | Charge |
|---|---|---|---|
| 1 | Feb. 14 | 4.76 | fresh: 15 hides |
| 2 | Feb. 15 | 9.86 | |
| 3 | Feb. 17 | 17.68 | 10 kg. lime; 15 hides |
| 4 | Feb. 18 | 19.04 | |
| 5 | Feb. 19 | 22.44 | |
| 6 | Feb. 20 | 24.48 | |
| 7 | Feb. 21 | 23.46 | 10 kg. lime; 15 hides |
| 8 | Feb. 22 | 24.82 | |
| 9 | Feb. 24 | 26.86 | |

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| No. | Date | Mg.$NH_3$ in 100 cc. | Charge |
|---|---|---|---|
| 10 | Feb. 25 | 28.22 | 10 kg. lime; 15 hides. |
| 11 | Feb. 26 | 28.22 | |
| 12 | Feb. 27 | 29.24 | |
| 13 | Feb. 28 | 27.2 | 2½ kg. sulphide; 15 hides |
| 14 | Feb. 29 | 28.22 | |
| 15 | Mar. 2 | 30.6 | |
| 16 | Mar. 3 | 22.63 | 1½ kg. sulphide; 15 hides |
| 17 | Mar. 4 | 25.16 | |
| 18 | Mar. 5 | 26.52 | |
| 19 | Mar. 6 | 27.2 | 1 kg. sulphide; 15 hides |
| 20 | Mar. 7 | 25.84 | |
| 21 | Mar. 9 | 26.52 | |
| 22 | Mar. 10 | 24.82 | 1 kg. sulphide; 15 hides |
| 23 | Mar. 11 | 24.48 | |
| 24 | Mar. 12 | 25.16 | emptied |

The lime liquors from a tannery were also examined. Here 5 vats of 11.5 cbm. capacity were used in series. In each vat 70 hides were hung and daily advanced to the next stronger. The limes were strengthened daily; No. 1 was freshly charged every 8–10 weeks, the others every 4–5 weeks.

*Charges Employed:*

| Vat. No. | Fresh charge Kg. lime | Kg. sulfid. | Strengthening Kg. lime | Kg. sulfid. |
|---|---|---|---|---|
| 1 | 300 | .. | 50 | .. |
| 2 | 350 | .. | 50 | .. |
| 3 | 400 | .. | 50 | .. |
| 4 | 400 | 15 | 50 | 6 |
| 5 | 400 | 15 | 50 | 6 |

*Analysis on Feb. 19:*

| Vat. No. | Fresh charged | Mg. $NH_3$ in 100 cc. |
|---|---|---|
| 1 | Jan. 13 | 6.13 |
| 2 | Jan. 20 | 13.60 |
| 3 | Jan. 27 | 25.84 |
| 4 | Feb. 3 | 33.32 |
| 5 | Feb. 10 | 35.00 |

The ammonia content in the liquors from the tannery school are seen to increase with the age of the lime; the slight decrease after addition of sulphide is probably due to dilution on bringing the hides from the soaks into the "sharpened" lime.

**Drum Stuffing.** *Gerber Zeitung*, 1908, [51], No. 139.—To obtain a uniformly retarded penetration of the fat it is important to properly moisten the leather, using the most water on the flanks and the least on the backs. The leather should soon be greased before the wetting has equalized. The drum should be heated in advance, then the leather let run 5–8 minutes to also warm up, else the fat will clot on adding, giving irregular greasing. The total quantity of grease mixture is added at once and rapidly, and then milled

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¾–1¼ hours. Drums are preferable which may be heated by a current of hot air. For upper leather the fat mixture should be 20–24% of the moistened stock, temperature 35–40° C. For belting leather requiring harder fats, 45–60° C. is used. On account of the heat, drum stuffing gives good results for belting only with good, sound leather.

**Bating in Acids.** *Gerber Zeitung*, 1908, [51], No. 140.—The treatment of the butts with warmed dilute acids (formic or lactic) can hardly be called a bating or even a substitute. The action of genuine bates depends upon micro-organisms. The mildest bate is from bran, then fowl dung, and dog dung the most powerful. Under circumstances however, when de-liming is more the object, acids may be used in place of bates; also when the tannery employs very soft water. A treatment with acid may precede the real bating, which then receives the hides well de-limed. After the hides are removed, the bath should still be weakly acid.

**The Tanning of Vache Leather.** *Gerber Zeitung*, 1908, [51], Nos. 144–146, 147, 148.—So many special qualities are required in this leather, that its manufacture calls for careful, thorough work in tanning.

2 to 3 days suffice to soak salted hides, 6 hours in the first water, 12 in a second water, then 12 and 12 to 24 in the fourth, care being taken to drain well in shifting. Dried hides require longer soaking; old water softens well and may be used according to the season if not too foul; it is best however with good river water to use this fresh, with proper renewal.

The liming should be carried through as rapidly as possible to avoid loss of hide. After dehairing, 2 days treatment with a weak bath of pure lime, swells the hide well for tanning; this is followed by pure water, then lactic acid; drums expedite the work.

Tanning in vats is first described. The preliminary tannage is first carried out in handlers and here the first requisite is to regularly strengthen the liquors; secondary decomposition products from tanning materials do not promote tanning or give a *permanent* swelling of the hide; this last has been sufficiently done in advance. Quebracho and myrabolams are generally used in combination with oak and pine barks; myrabolams, being strong in sugar, should be used in moderation. A liquor drawn off, lay-away vats should not be used direct before refreshing with new bark. Acids should not be added. From the vats the hide goes immediately into the layaway, containing a liquor of 3½ to 4°B., remaining here about three weeks. A second layaway of 4 to 4½° containing more quebracho should complete the tannage in four weeks. In vat tannage, the liquors should be cold, never above 20°R. In many tanneries the vat process is shortened and the tanning completed in drums with good results.

Direct tanning in drums is next discussed. In this rapid process with strong liquors care must be taken not to overdo in this direction since the pores of the leather may become clogged, especially when the fore-tanning has been slight. The motion however tends to open the leather and the heat generated quickens the reaction. The preliminary tannage is carried out in handlers, the same principles governing as in vat tanning proper. The liquor for the drums is not added at once but at least in three stages

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beginning with 6 to 7°B. and ending, at the longest, in three days with 9 to 10°. The leather is then placed a few hours in a weak liquor and finally two to three hours in pure water. Vat-tanned leather needs merely rinsing. After some airing, the grain is oiled, and the leather left to dry sufficiently for the currying operations which are described.

**Tanning and Dyeing.** W. FAHRION. *Chemiker Ztg.*, through *Collegium*, 1908, No. 311, pp. 173-8.—The author finds Stiasny's criticisms of his tanning theory as a chemical process involving oxidation of the hide fibre to be sound and justified by the evidence to date. (*Chem. Ztg.*, 1907, 1218, 1270). He is now able to bring forward further evidence but first considers in some detail the theories relating to dyeing since Stiasny has made use of these in the discussion.

Two views are held regarding the nature of dyeing, it being either a chemical or a physical process. The principal arguments for the chemical theory are as follows: From wool, an acid may be separated the aqueous solution of which is precipitated by all substantive dye-stuffs as well as tannic and chromic acids. The maximum amounts of certain dye-stuffs taken up by wool are proportional to their molecular weights. (Knecht; *Ber. deutsch. chem. Ges.*, [21] 1556, 2804; [22] 1150; [35] 1022.) Animal fibres are hydrolyzed on dyeing, acting both as acids and bases with salt formation. (Suida; *Ztsch. Farbenind.*, [6], 4.) In support of the opposed physical theory, v. Georgievic (*Chem. Ztg.*, (1902) 129) finds that dyes are taken up by the fibre in accordance with the laws governing adsorption and not according to stochiometric rules. Moreover the fibre takes up many inorganic colloids independent of their chemical nature, and finally the fibre itself may be substituted by an inorganic colloid without altering the quantitative character of the adsorption. (Biltz; *Ber. deutsch. chem. Ges.*, [37] 1766; [38] 2903, 2973, 4143.)

Of the earlier writers who have declared for a chemical union between hide and tan-stuff, only A. Müntz (*Compt. rend.* [69] 1309) is to be named; he found that an approximately constant amount of each tan-stuff is absorbed. Von Schroeder and Paessler confirm this for upper limits but since the amount varies with concentration, they like Knapp, explain tanning as a physical process. (v. Schroeder's *Gerberchemie.*) Th. Körner, (*Jahrbesber. Gerberschule*, 1899, 1900, 1903) found this confirmed in the failure of electrolytic dissociation of hide fibre or tan-stuff, hence incapability of salt formation. This seems remarkable in the light of Suida's work on dyes; every tannage is preceded by an acid treatment (bating) and therefore a hydrolysis of hide fibre is even more probable than one of wool. The author has made comparative trials in dyeing hide-powder and short cut (1 mm.) woolen yarn and found the hide much deeper dyed; he therefore thinks Suida's conclusions may be applied direct to hide.

The lack of stochiometric relations need not argue against chemical union, for tanning is more or less superficial and the interior of a mass of fibre, however small may be unchanged. The proportion between tanned and untanned molecules remains unknown and this principle affects all experiments on which physical theories are based.

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Moreover the theory that the hide molecule contains not only one but different "tannophore" groups permits a quantitative variation in genuine chemical absorption. Herzig, Freundlich, Heidenhain, Zacharias and other investigators have concluded that both physical and chemical changes take place in dyeing. The author's view is that according to our present knowledge, in the first stage the fibre acts as a colloid, adsorbing the dye-stuff, in the second, it is hydrolyzed and enters into chemical reaction with the dye-stuff, and under favorable conditions, even in stochiometrical proportions. This may also be applied to leather formation and in that sense he agrees with Stiasny; insisting upon chemical action in the second stage.

**An Improved Extractor for Tanning Materials.** L. SHEARD. *Collegium*, 1908, 319, pp. 275, 276.—A modification of the Procter percolator extractor; the water used for extracting is fed from an elevated reservoir, the tubes carrying it from the reservoir to the extracting vessel being coiled around this vessel as it stands submerged in the water-bath. The water is thus heated to the temperature of the water-bath before it flows on the tanning material; the flow is regulated by a screw cock, and another screw cock regulates the amount of solution coming from the extracting vessel. This apparatus embodies the principle of the Teas percolator extractor (this JOURNAL, 1906, 3, 181 to 183).

**Deterioration of Leather Under the Influence of Gas Fumes.** M. C. LAMB. *J. Soc. Dyers and Col.*, 1908, 24, 160-166.—The conclusions of the author confirm those of the committee of the Society of Arts, that next to sumac, algarobilla, chestnut extract, and myrabolams are the most suitable tannages for bookbinding leathers. Chrome tanned leather is also mentioned. The results of the investigations show that shellac and egg-albumen are the best finishes for this class of leather. Japanned leather also gives good results.

## PATENTS.

**Leather Splitting Machine, U. S. Patent No. 894,850.** To F. J. NASH, Somerville, Mass. An improved splitting machine.

**Friable Vegetable Dye and Process of Making Same, U. S. Patent No. 894,965.** To F. J. MAYWALD, New York. Similar process to that described under U. S. Patent No. 894,277. (JOURNAL, 1908, 296).

**Black Stain for Leather, Fr. Patent 383,657.** To J. M. COMBE AND M. DENIS. Denatured alcohol, 665 grams; aniline black, 15 grams; ivory black, 40 grams; sandarac, 10 grams; umber, 30 grams; gum lac, 20 grams; all to one liter.

**Improvements in Machines for Dehairing Hides, Fr. Patent No. 383,848.** To G. H. KELLER.

**Glue-Testing Process and Apparatus, U. S. Patent 896,191. To C. M. ZIMMERMAN, Cincinnati, Ohio. A method for testing the strength of glue, and apparatus for making the test.**

**Leather Stretcher, U. S. Patent No. 896,387.** To W. F. HYSON and C. G. BARNSTEAD, Phila., Pa. An improved adjustable drying frame.

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**Apparatus for Evaporating and Concentrating Liquids, U. S. Patent No. 896,460.** To C. L. PRACHE AND C. G. V. BOUILLON, Paris, France. An improved tubular vacuum pan.

**Composition of Matter, U. S. Patent No. 898,044.** To A. E. GOOCH, Campello, Mass. A "filler" for reinforcing the leather soles of welted shoes, consisting of ground cork and "apparatine".

**Evaporator, U. S. Patent No. 898,147.** To E. VON SEEMEN, Rheinfelden, Switzerland. An improved vertical tube evaporator.

**Process of Tanning. French Patent No. 376,840.** E. PERRST. The butts are treated with solutions of sulphate magnesia and alum, then of gambier, at 15-18°, prior to the usual tannage.

**Leather Working Machine. French Patent No. 383,176.** A. DELIGNON.

**Machine for Shaving and Splitting Leather. French Patent, No. 387,397.** A. G. MOENUS.

**Process for Bating Hides. French Patent No. 387,950.** ROHM. An aqueous extract of the pancreas of animals is used, the action being claimed to be similar to that of dog dung fermentation.

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## The American Leather Chemists Association

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## FIFTH ANNUAL MEETING ANNOUNCEMENT.

**Boston, Mass., Thursday, Friday and Saturday, Nov. 12th, 13th and 14th.**

The Hotel Brunswick, Copley Square, corner Clarendon and Boyleston sts. has been selected as headquarters. Rates are as follows: Rooms $2 per day and upwards. Room with bath $2.50 per day and upwards. Rooms when occupied by two persons $1 per day additional. American plan; $4 per day and upwards.

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This hotel is two blocks from the Back Bay Station of the N. Y. N. H. & H. R. R. and the same distance from the Huntington Ave. Station of the B. & A. R. R.

Sessions will be held morning and afternoon and on one evening as follows: Thursday morning; President's address, reports of the Secretary-Treasurer and consideration of Committee reports.

Thursday afternoon; This session will be devoted to non-technical matters with addresses of representatives from the Tanning Industry, Shoe Manufacturers and others.

Thursday evening; Prof. H. S. Graves, Director of the Yale Forestry School will deliver an address. This session will be held at the Mass. Institute of Technology.

Friday morning; Consideration of Committee reports and Technical papers.

Friday afternoon; Continuation of same, or if time permits, visits to Harvard University or a shoe manufacturing establishment.

Friday evening; Bohemian Supper.

Saturday morning; Unfinished business, election of Officers, etc.

The meetings of the Association, with the exception of the one on Thursday evening, will be held at the Hotel Brunswick.

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## THE CHROMING AND ACIDITY OF HIDE-POWDER.[1]

*By H. C. Reed.*

The Committee having in charge the question of the chroming and acidity of hide powder herewith submit the following report:

The Chairman sent the following instructions to members of the Committee:

1. Using Teas Standard Hide-powder, acidify to the following definite acidities, determining the original acidity of the powder by the method of Small (JOUR. A. L. C. A., Vol. III, No. 3, pg. 77).

[1] Report of the 1908 Committee.

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(a) 15 cc. N/10 NaOH required for 10 gms. absolutely dry powder.
(b) 20 cc. N/10 NaOH required for 10 gms. absolutely dry powder.
(c) 7.7 cc. N/10 NaOH required for 10 gms. absolutely dry powder.

When acid is added to attain the required acidity it is requested that the three acids, hydrochloric, acetic and formic, be used for each acidification. When the acidity desired is less than the acidity of the powder NaOH shall be used. The requisite amount of acid or alkali must be determined upon a separate portion of the hide-powder and sufficient time allowed for complete absorption of the acid.

2. The powders acidified as in (1) shall be chromed as follows:

(d) By the A. L. C. A. official method.

(e) By the official method of the I. A. L. T. C., as follows:—

2 gms. of crystallized chromic chloride ($Cr_2Cl_6.12H_2O$) per 100 gms. of dry powder is dissolved in water and made basic with 0.6 gms. of $Na_2CO_3$ by the gradual addition of 11.25 cc. N/1 solution. This solution is added to the powder and the whole churned slowly for one hour. The powder is then squeezed in linen and squeezed after the addition of each wash-water, until on adding to 50 cc. of the filtrate, one drop of 10 per cent. $K_2CrO_4$ and four drops N/10 $AgNO_3$, a brick-red color appears. Four or five squeezings are usually sufficient. The powder is then squeezed to contain 70-75 per cent. water, and used as directed by the official A. L. C. A. method.

3. The powders acidified and chromed as directed in (1) and (2) shall be used to detannize the following extract solutions:—

(f) Chestnut ..... 15 gms. per liter.
(g) Hemlock ..... 16 gms. per liter.
(h) Quebracho ..... 12 gms. per liter.

It is requested that careful note be made of the appearance of all the non-tannin filtrates and of the dried residues, the latter for the purpose of ascertaining whether with increase of acidity there is increased charring effect. It is also desirable that it be ascertained, if possible whether the non-tannin filtrates from

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the I. A. L. T. C. method of chroming contain a greater or less proportion of chloride than the non-tannin filtrates from the A. L. C. A. method contain of sulphates. In this connection the amounts of chlorides and sulphates originally present in the extract solutions must be taken into account. It is suggested that the latter point might be determined by detannizing a solution of gallotannic acid free from sulphates and chlorides. The blank test with water is of little value in the writer's estimation.

4. *A modified method*:—The powder is chromed according to the official A. L. C. A. method, squeezed and a portion of the filtrate evaporated to determine the solubles. (The portion evaporated must necessarily be filtered to a clear solution before evaporation). The powder, without washing, is used to detannize in the usual manner, and the non-tannins corrected for the solubles contained in the liquor held by the powder. It is recommended that the powder be given a preliminary washing with distilled water prior to chroming. The results from this method are to be compared to the official A. L. C. A. method. Comments on this method are requested.

It is especially desired that the opinion of collaborators be given as to the relative value of the A. L. C. A. and I. A. L. T. C. methods of chroming, whether one method is superior to the other in accuracy, speed or versatility.

The results obtained are included in the following tables:—

TABLE I.

SHOWING EFFECT OF ACIDIFICATION OF HIDE-POWDER UPON NON-TANNINS.

*Chestnut*—

| | 7.7 acid | | HCl — 15° | | Acetic — 15° | | Formic — 15° | |
|---|---|---|---|---|---|---|---|---|
| | A.L.C.A. | I.A.L.T.C. | A.L.C.A. | I.A.L.T.C. | A.L.C.A. | I.A.L.T.C. | A.L.C.A. | I.A.L.T.C. |
| Small | 20.30 | 18.94 | | | | | 20.26 | 19.40 |
| Fox | 20.16 | 20.31 | 20.09 | 20.28 | 20.05 | 20.11 | 20.14 | 19.91 |
| Wisdom | 20.07 | | 20.20 | | 19.91 | | 20.03 | |

| | HCl — 20° | | Acetic — 20° | | Formic — 20° | |
|---|---|---|---|---|---|---|
| | A.L.C.A. | I.A.L.T.C. | A.L.C.A. | I.A.L.T.C. | A.L.C.A. | I.A.L.T.C. |
| Small | 20.33 | 18.92 | 20.26 | 18.70 | 20.45 | 19.03 |
| Fox | 20.65 | 20.07 | 20.53 | 20.18 | 20.18 | 20.14 |
| Wisdom | 20.25 | | 20.15 | | 20.11 | |

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TABLE I.—(*Continued*).

| | 7.7 acid | | HCl — 15° | | Acetic — 15° | | Formic — 15° | |
|---|---|---|---|---|---|---|---|---|
| *Hemlock*— | A.L.C.A. | I.A.L.T.C. | A.L.C.A. | I.A.L.T.C. | A.L.C.A. | I.A.L.T.C. | A.L.C.A. | I.A.L.T.C. |
| Small | 16.11 | 15.06 | | | | | 15.97 | 15.63 |
| Fox | 15.87 | 17.44[1] | 16.42 | 16.35 | 16.28 | 16.64 | 16.13 | 16.35 |
| Wisdom | 16.08 | | 15.87 | | 16.23 | | 16.13 | |

| | HCl — 20° | | Acetic — 20° | | Formic — 20° | |
|---|---|---|---|---|---|---|
| | A.L.C.A. | I.A.L.T.C. | A.L.C.A. | I.A.L.T.C. | A.L.C.A. | I.A.L.T.C. |
| Small | 15.90 | 15.23 | 16.04 | 15.16 | 15.82 | 15.23 |
| Fox | 16.67 | 15.73 | 16.19 | 16.06 | 17.56[2] | 15.77 |
| Wisdom | 15.47 | | 15.82 | | 15.62 | |

| | 7.7 acid | | HCl — 15° | | Acetic — 15° | | Formic — 15° | |
|---|---|---|---|---|---|---|---|---|
| *Quebracho*— | A.L.C.A. | I.A.L.T.C. | A.L.C.A. | I.A.L.T.C. | A.L.C.A. | I.A.L.T.C. | A.L.C.A. | I.A.L.T.C. |
| Small | 11.94 | 10.62 | | | | | 11.69 | 11.59 |
| Fox | 11.70 | 12.35 | 11.50 | 12.22 | 11.58 | 12.01 | 11.46 | 11.88 |
| Wisdom | 11.24 | | 11.17 | | 11.07 | | 11.05 | |

| | HCl — 20° | | Acetic — 20° | | Formic — 20° | |
|---|---|---|---|---|---|---|
| | A.L.C.A. | I.A.L.T.C. | A.L.C.A. | I.A.L.T.C. | A.L.C.A. | I.A.L.T.C. |
| Small | 11.39 | 10.03 | 11.61 | 10.39 | 11.55 | 10.47 |
| Fox | 11.60 | 11.75 | 11.65 | 12.08 | 11.64 | 12.00 |
| Wisdom | 11.13 | | 11.32 | | 11.04 | |

[1] Cloudy: moisture in hide-powder below limit.

[2] Cloudy.

TABLE II.

SHOWING NON-TANNINS USING HIDE-POWDER UNWASHED AFTER CHROMING AND CORRECTING FOR SOLUBLES.

| | Official method | Per cent. with wash water correction | Weight of wash water residue | Wash water correction | Weight of ash from wash water residue | Ash correction | Per cent. with ash correction |
|---|---|---|---|---|---|---|---|
| *Chestnut*— | | | | | | | |
| Small | 20.32 | 20.15 | .0532 | .0076 | | | |
| Fox | 20.63 | 18.90 | | | | | |
| Wisdom | 20.27 | 18.52 | .2288 | .0312 | .0572 | .0078 | 20.32 |
| *Hemlock*— | | | | | | | |
| Small | 16.07 | 15.68 | .0532 | .0076 | | | |
| Fox | 15.94 | 14.31 | | | | | |
| Wisdom | 16.08 | 13.88 | .2288 | .0312 | .0572 | .0078 | 15.59 |
| *Quebracho*— | | | | | | | |
| Small | 11.72 | 11.34 | .0532 | .0076 | | | |
| Fox | 11.65 | 9.48 | | | | | |
| Wisdom | 11.16 | 8.93 | .2288 | .0312 | .0572 | .0078 | 11.20 |

TABLE IIA.

SMALL. SHOWING SAME AS TABLE II.

| | Official method | Per cent. with wash water correction | Weights of wash water residue |
|---|---|---|---|
| Oak bark | 21.54 | 21.25 | .0459 |
| Hemlock | 17.04 | 16.94 | .0459 |
| Quebracho | 11.44 | 11.05 | .0459 |
| Chestnut wood | 14.96 | 14.94 | .0459 |

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TABLE III.

SHOWING COMPARATIVE NON-TANNINS BY THE OFFICIAL AND RAPID METHODS OF CHROMING.

| | Small | | Wisdom | |
|---|---|---|---|---|
| | Official method | One hour's chroming | Official method | One hour's chroming |
| Chestnut | 20.32 | 20.16 | | |
| Hemlock | 16.07 | 15.59 | | |
| Quebracho | 11.72 | 11.69 | | |
| Chestnut ext. No. 1 | | | 15.51 | 15.36 |
| Chestnut ext. No. 2 | | | 14.08 | 13.96 |
| Chestnut ext. No. 3 | | | 14.21 | 14.02 |
| Chestnut ext. No. 4 | | | 14.35 | 14.28 |
| Chestnut ext. No. 5 | | | 13.55 | 13.40 |
| Oak bark ext. No. 1 | | | 19.80 | 19.78 |
| Oak bark ext. No. 2 | | | 18.54 | 18.43 |
| Chestnut ext. No. 6 | | | 12.36 | 12.29 |

TABLE IV.

SMALL. SHOWING EFFECT UPON NON-TANNINS OF REDUCING. HIDE-POWDERS OF VARYING TEXTURE AND ACIDITY TO THE SAME ACIDITY.

| | Official chroming | | | | International chroming | | | |
|---|---|---|---|---|---|---|---|---|
| | K | S | K′ | S′ | K | S | K′ | S′ |
| Chestnut | 19.93 | 19.91 | 20.17 | 20.05 | 21.24 | 19.53 | 21.99 | 19.99 |
| | 19.85 | 20.12 | 20.06 | 19.97 | 21.38 | 19.50 | 21.85 | 19.80 |
| Av | 19.89 | 20.01 | 20.12 | 20.01 | 21.31 | 19.52 | 21.92 | 19.90 |
| Hemlock | 16.68 | 16.04 | 15.43 | 15.32 | 17.73 | 16.21 | 16.44 | 15.25 |
| | 16.82 | 16.02 | 15.51 | 15.32 | 17.89 | 16.52 | 16.38 | 15.32 |
| Av | 16.75 | 16.03 | 15.47 | 15.32 | 17.81 | 16.37 | 16.41 | 15.29 |
| Quebracho | 11.97 | 11.56 | 11.92 | 11.71 | 12.72 | 11.86 | 12.81 | 11.94 |
| | 12.00 | 11.63 | 11.90 | 11.99 | 12.72 | 11.85 | 12.83 | 11.94 |
| Av | 11.99 | 11.60 | 11.91 | 11.85 | 12.72 | 11.86 | 12.82 | 11.94 |
| Per cent. water in wet h.p. | 74.5 | 74.2 | 74.6 | 75.1 | 73.6 | 73.4 | 75.1 | 74.3 |
| Wt. wet. h.p. to 200 cc | 45.5 | 45.3 | 45.5 | 46.0 | 45.5 | 45.2 | 46.0 | 45.5 |
| Wt. dry h.p | 11.6 | 11.7 | 11.6 | 11.5 | 12.0 | 12.0 | 11.5 | 11.7 |

K = hide-powder No. 1 of natural acidity 15.9° reduced to 7.1° by addition of N/10 NaOH.

S = hide-powder No. 1 of natural acidity 15.9°.

K′ = hide-powder No. 2 of natural acidity 7.1°.

S′ = hide-powder No. 2 of natural acidity 7.1° acidified to 15.9° with N/10 formic acid.

All the hemlock non-tannin filtrates with hide-powder No. 1 were colored and opalescent.

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Concerning the results of his investigations, Mr. Small has the following to say:

"The following results were obtained using Teas' 1908 standard hide-powder, except where otherwise stated. Each series was conducted under identical conditions and using the same analysis solution. In Series III two hide-powders differing greatly in physical characteristics were used. Hide powder No. 1. was very fibrous and granular, with a more or less greasy feel and of a yellowish white color; hide-powder No. 2 was very woolly and of a brownish color. Both these samples had been in the writer's laboratory for a number of years and both, but more particularly sample No. 2, had become soluble to such an extent that the amounts of each used for detannizing, calculated from the air dry weight, fell below the official limit owing to loss in washing. Hide-powder No. 1 moreover, under these conditions failed to detannize the hemlock solution, the non-tannin filtrates all being somewhat colored and strongly opalescent.

An attempt was made to estimate the relative amounts of sulphate and chloride in the non-tannin filtrates from the two methods of chroming in Series I by comparing the opacity of the filtrates after precipitating with hydrochloric acid and barium chloride and nitric acid and silver nitrate respectively, with solutions of sodium sulphate and sodium chloride of known strength which had been precipitated under precisely similar conditions. The amounts of sulphate seemed to lie between one part in 2000 and one in 10,000; and the amounts of chloride between one in 10,000 and one in 20,000. No general law governing the amounts of sulphate and chloride in the non-tannin filtrates when hide-powders of different acidities and chromings were used, could be discovered by the writer.

A study was also made of the different residues by both the writer and his two assistants in an attempt to discover whether different degrees of charring or caramelization were detectable. While there was considerable difference in the appearance of the residues, particularly as between the official and the international chroming, no general rule governing the degree of caramelization as between hide-powders of different acidities, and those of the same acidity but acidified with different acids, was discoverable.

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In all cases where acid or alkali was added the required amount was added to the soak water and the mixture allowed to stand one hour with occasional stirring before the chrome solution was added. As not enough chromic chloride was supplied by the Chairman for all the above work, the so-called dry chromic chloride used by the writer in his Committee work on the acidity of hide-powder last year was used for chroming in the same manner as described in his report. (JOURNAL A. L. C. A., Vol. II, No. 10, pgs. 347-355).

The above results are of interest as throwing some light on the question of the relation between the weights of the non-tannin residue and the acidity of the hide-powder. The writer is inclined to the belief that too high and too low acidities both lead to high non-tannin weights and that this is the explanation of the different results obtained by the writer and Messrs. Reed, Bennett and others in the past. In the work of the Committee last year on the acidity of hide-powder for instance, hide-powders of much higher acidity than any of those employed in the present work were used and these lead to higher results than those of less acidity; these latter, however, were almost as acid as the most acid hide-powder used in the present work.

The results further show rather conclusively that the values obtained by the basic chloride method of chroming are effected much more seriously by variations in the physical character or in the acidity of the hide-powder used, than are those by the chrome alum method of chroming.

As between the Official and International methods of chroming, the writer can see nothing in favor of the International method except possibly the use of the smaller amount of soak water and the shortened time of chroming. The practical manipulation of the hide-powder is more tedious by the International method. In no case did the three or four washings suffice to give a wash water meeting the required tests, in all cases from eight to twelve washings were found necessary. The chrome solution is more of a nuisance to prepare. The non-tannin residues apparently show much more of a charring or caramelization effect. Finally, and which is the most serious defect in the International method, the non-tannin results are seriously

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affected by comparatively small differences in the acidity or physical character of the powder.

There seems no real reason why the points of advantage, if so found, of the International method should not be incorporated in the Official method and with this in view the writer tried chroming the hide-powder for one hour after digesting with only ten times its weight of water. The results were promising and the writer regrets that he has, up to the present, been unable to carry the work further.

The serious objections to method No. 4 would seem to be the uncertain effect of the mineral constituents of the liquor carried into the analysis solution by the hide-powder and the possibility that a uniform mixture of this liquor between the analysis solution and the hide-powder does not take place. The results shown above are inclined to be low and this may well be due to either one of the above causes."

Mr. Fox has the following to say:

"The different non-tannin filtrates from the Chestnut and Quebracho extracts were very similar in appearance. The filtrates from the hemlock extract were all slightly opalescent, especially those from hides of acidity 7.7° and formic 20°, in which the moisture was too low. Probably these results should be omitted. The clearness of these filtrates increased with the increase of acidity in the hide with the exception of hide 20° acidity, A. L. C. A. method. The residue obtained by the different methods all looked alike.

By mistake in modified method No. 4, the hide was not washed before chroming, and as a result, the filtrates from the squeezing contained considerable soluble hide, so that the results obtained are probably not of much account."

The Chairman concludes from the results shown in Table I that the acidification of hide-powder with the volatile acid has but little effect upon the non-tannins if the Official method is used and the acidity of the hide-powder kept within certain limits. He agrees with the conclusions of Small that acidities above or below certain limits both tend to raise the non-tannin figure, but from different causes. Low acidity in hide-powder results in failure to detannize to the same degree as a higher acidity,

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while an extreme acidity raises the non-tannins from the incomplete volatility of the acid.

As it is evident that varying acidity in hide-powder may lead to disagreeing results in non-tannins, it would seem wise to specify in our method a certain definite acidity. As it seems impossible in the manufacture of the powder to accomplish this, the Chairman would recommend that the individual analyst do so by the use of the required amounts of caustic soda or acetic or formic acids. The necessary amount of acid or alkali should be added at least one hour before the addition of the chroming solution. The Chairman would recommend an acidity requiring 1 cc. N/10 NaOH for 1 gram of the air dry powder. This is higher than the International method allows as an extreme acidity, but lower acidity will almost certainly result in cloudy non-tannin filtrates with extracts such as oak and hemlock.

The results from the I. A. L. T. C. method of chroming, as shown in Table I, would indicate that slight variations in the degree of acidity of the hide-powder lead to greater variations in the non-tannins than is shown in our Official method under like conditions, but the returns are somewhat too meagre to permit of any very definite conclusions on this point.

Respecting the proposed method (4), suggested recently by Prof. Procter, the results shown in Table II, seem to prove that wide variations are liable to result from the proportion of soluble hide remaining in the wash water. It must be remembered, however, that our Official method of chroming was employed and not the International method on which Prof. Procter based his conclusions, but even under the varying conditions it appears likely to the Chairman that under any circumstances the method will be open to the objection noted. Before the day of chrome hide-powder much of the difficulty experienced in the non-tannin estimation came from the soluble matters of the hide, and it would seem that even a drastic washing of the powder previous to chroming would not be effective in removing all soluble hide as shown by a test of the wash water after chroming. If soluble hide is present in the wash water, and it is the Chairman's experience that it always is, the factor for correction of the non-tannins must be incorrect, lowering the results from the fact

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that the soluble hide does not appear in the residue of non-tannins but is precipitated and removed by the tannin.

Table III indicates that the time of chroming can be reduced to one hour without materially affecting the non-tannin figures. This was shown by Mr. Alsop as early as 1902. (U. S. Department of Agriculture, Bulletin No. 67, pg. 141.) Mr. Small's results are by chroming one hour without shaking and Mr. Wisdom's by chroming one hour with shaking. It appears to the Chairman better to use mechanical agitation when the time of chroming is so greatly lessened as such will tend to bring the hide and chroming solution into more intimate contact. There is a decided advantage in the rapid chroming method when the analysis of liquors is considered and the Chairman recommends that it be taken under advisement.

The advantage that the International method of chroming may have over our Official method is not apparent to the Chairman. As before noted, the former method has the seeming disadvantage of the greater sensitiveness of the resulting chromed powder to acidity as reflected in the variations in non-tannin figures.

Since rapid chroming is affected by the use of chrome alum there is evidently no advantage in this particular from the employment of chrome chloride.

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## DETERMINATION OF WATER IN SOD OILS.

*By Dr. Louis E. Levi and E. V. Manuel, S. B.*

The question, whether the sand or Fahrion method is more accurate for the determination of water in sod oils and moellons, has been before the chemists employed in the leather industry for quite a long while. Not wishing to discuss the pros and cons of each respective method, we desire to give the method employed by us, which has yielded excellent and most satisfactory results. The sod oil or moellon is placed in a weighed flask (see illustration) with some washed and dry sand and placed in a Victor Meyer constant heater filled with Toluol boiling point 107°C. The upper end of the pipette is connected with a carbonic acid cylinder or apparatus and the stream turned

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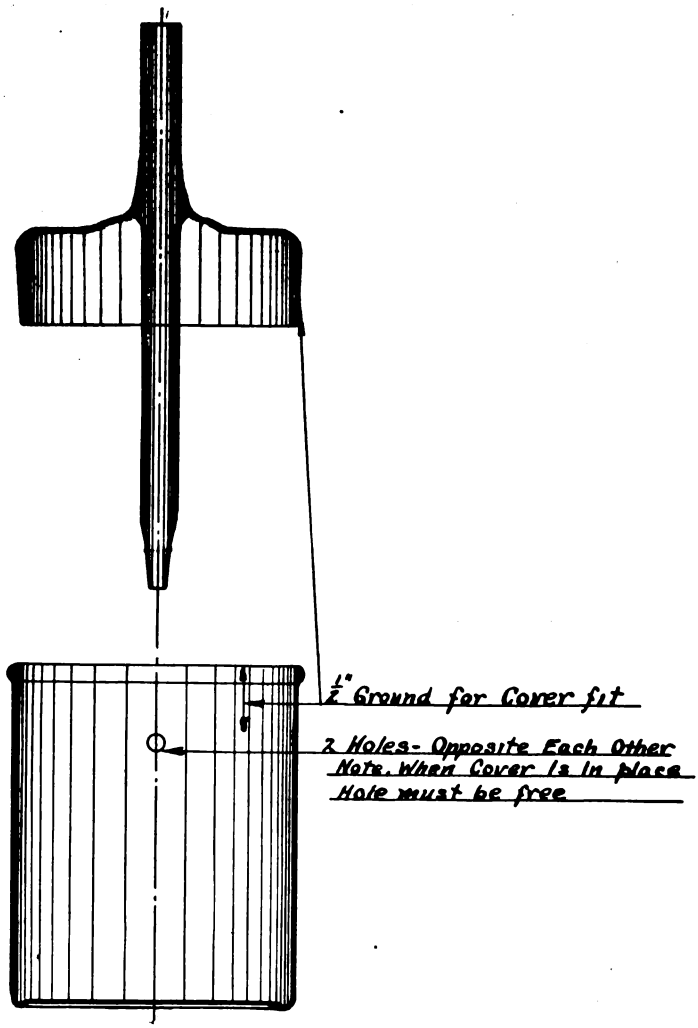
on so as to pass through one wash bottle containing concentrated sulphuric acid and then through a wash bottle containing glass wool. The carbonic acid gas is regulated so as to pass




through the bottles about two bubbles per minute. Heat is now applied to the drying apparatus and the oil and sand mixture allowed to remain under these conditions about three hours when the glass weighing bottle pipette is placed in the desicca-

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tor to cool, then weighed. The weight will be found to be constant in about this time.

The following is a comparison of the results obtained by the Fahrion and our method:—

| | Fahrion $H_2O$ Per cent. | $CO_2$ method $H_2O$ Per cent. |
|---|---|---|
| I | 25.35 | 23.87 |
| II | 23.43 | 24.50 |
| III | 25.34 | 25.61 |
| IV | 43.20 | 43.31 |
| V | 20.86 | 21.01[2] |
| VI | 22.50 | 22.02[2] |
| VII | 47.55[1] | 42.61[2] |

[1] Nearly impossible to get even approximate results, due to spurting.
[2] Crucible method.

We have also tried the same method with a variation of placing a weighed platinum crucible into the weighing bottle without the use of sand and got very good and accurate results. The only objection to the crucible method is:—a little oil sticks to the end of the pipette which must be washed off with petroleum ether or dichloraethylene, added to the contents of the crucible, evaporated and weighed. As the oil is very difficult to dissolve and evaporation very tedious the investigation of the crucible method has been deferred. With the carbonic acid method the ash can not be obtained from the same sample but in the crucible method ash and moisture can be obtained from the original sample. There is absolutely no spurting and no oxidation of the oils. The temperature of drying is always constant and the amount of water contained in the oil does not affect the accuracy of the method. We have also adopted the $CO_2$ method for soaps, substituting dry air in place of the carbon dioxide with excellent results.

## ACIDITY IN TANNERY LIQUORS.[1]

*By W. K. Alsop.*

The members of this Committee were requested to experiment with the following methods in such ways as seemed best to them,

1. Procter's lime water method, attention being called to

[1] Report of 1908 Committee.

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the paper by H. G. Bennett and C. D. Wilkinson, J. S. C. I. November 30th, 1907.

2. A gelatine precipitation method used by F. H. Small, which is as follows:—

"As practiced by me at present, to a certain number of cc. of liquor are added a certain number of cc. of 2 per cent. solution of gelatine in water, the relative number of cc. being determined by the strength of the liquor. In each case there is in the end 70 cc. of solution, the proportions varying from 60 of gelatine and 10 of liquor to 10 of gelatine and 60 of liquor. I add about a gram of kaolin to the mixture and filter, then titrate 50 cc. of the filtrate. In general the filtrate is perfectly clear, but it makes no material difference in case it happens to be a little cloudy. I titrate with N/10 alkali and up to recently have used a spot test on turmeric paper, to get the end point. Lately I have been using a logwood solution to get the end point and with a rather good degree of success. The method of using the logwood which I found advantageous was as follows:—

"In stirring the liquor during the titration a foam collects on the top and on running a drop of logwood solution down the side of the beaker in which the titration is being carried on, the color change is very clearly seen as the drop passes through the foam. The titration as I conduct it practically makes use of the Procter method for I use N/10 barium hydrate for my alkali. This gives a precipitate in the clear filtrate the same as lime does and as the filtrates are practically never wholly free from tannin, the alkali can be run in rapidly until there are evidences of cloudiness, then use the logwood solution to get an exact end point, as outlined above."

3. Hoppenstedt's Quinine method (this JOURNAL, Sept., 1907, page 304).

4. Charcoal method.

5. Reed's Alcoholic Gelatine-Hematein and Basic Dye-Hematein methods (this JOURNAL, March, 1908, pages 85-91).

The following reports were received from members of the Committee.

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## W. P. MAXWELL.

### Methods Used.

1. Lime water method.....Procter's
2. Calcium sucrate solution,
3. Gelatine precipitation method.....F. H. Small's
4. Improved quinine method.....Hoppenstedt's
5. Charcoal method.....Official
6. Alcoholic gelatine-hematein method.....Reed's
7. Basic dye-hematein method.....Reed's

### Liquors Used.

A. Fresh hemlock.
B. Weak spent union.
C. Fresh oak.
D. Chestnut extract, made from an old sample of chestnut oak extract.
E. Union spent layaway.
F. Tannic acid and water, about 0.4 per cent. tannin.

In the following table the figures [1], [2], [3] indicate the following: [1], difficult to determine end point; [2], nearly impossible to determine end point; [3], impossible to determine end point:

| | Lime water | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | 10 cc. liq. no water Per cent. | 10 cc. liq. 25 cc. water Per cent. | 10 cc. liq. 50 cc. water Per cent. | 2. Calcium sucrate Per cent. | 3. Gelatine precipt. Per cent. | 4. Improved quinine Per cent. | 5. Charcoal Per cent. | 6. Alcoholic gelatine Per cent. | 7. Basic dye lemon yellow O Per cent. |
| A/1.. | 0.27[2] | 0.30 | 0.34 | 0.36 | 0.25 | 0.34 | 0.34 | 0.26 | 0.29 |
| A/2.. | 0.76 | 0.77 | 0.78 | 0.82 | 0.73 | 0.83 | 0.88 | 0.73 | 0.80 |
| A/3.. | 1.22 | 1.23 | 1.25 | 1.24 | 1.18 | 1.35 | 1.34 | 1.24 | 1.20 |
| A/4.. | 1.24 | 1.26 | 1.27 | 1.26 | 1.18 | 1.35 | 1.34 | 1.24 | 1.20 |
| B/1.. | 0.22 | 0.23 | 0.24 | 0.26 | 0.18 | 0.33 | 0.29 | 0.22 | 0.23 |
| B/2.. | 0.71 | 0.72 | 0.74 | 0.78 | 0.67 | 0.94 | 0.74 | 0.74 | 0.76 |
| B/3.. | 1.20 | 1.21 | 1.22 | 1.21 | 1.19 | 1.39 | 1.22 | 1.23 | 1.23 |
| B/4.. | 1.20 | 1.21 | 1.22 | 1.21 | 1.18 | 1.36 | 1.17 | 1.23 | 1.23 |
| C/1.. | 0.15[2] | 0.20 | 0.23 | 0.21[2] | 0.19 | 0.33 | 0.37 | 0.12 | 0.11 |
| C/2.. | 0.63[1] | 0.64[1] | 0.67 | 0.60[2] | 0.63 | 0.72 | 0.88 | 0.60 | 0.62 |
| C/3.. | 1.12[1] | 1.12[1] | 1.13[1] | 1.12[2] | 1.09 | 1.28 | 1.31 | 1.05 | 1.08 |
| C/4.. | 1.12[1] | 1.12[1] | 1.13[1] | 1.12[2] | 1.08 | 1.28 | 1.37 | 1.05 | 1.15 |
| D/1.. | [3] | [3] | [3] | [3] | 0.19 | 0.39 | 0.37 | 0.22 | 0.27 |
| D/2.. | [3] | [3] | 0.69[2] | [3] | 0.65 | 0.83 | 0.85 | 0.77 | 0.74 |
| D/3.. | [3] | [3] | 1.05[2] | [3] | 1.13 | 1.31 | 1.37 | 1.21 | 1.22 |
| D/4.. | [3] | [3] | 1.19[2] | [3] | 1.18 | 1.41 | 1.40 | 1.28 | 1.23 |
| E/1.. | 0.56 | 0.57 | 0.58 | 0.53 | 0.54 | 0.66 | 0.68 | 0.58 | 0.57 |
| E/2.. | 1.11 | 1.13 | 1.13 | 1.05 | 1.01 | 1.23 | 1.17 | 1.06 | 1.07 |
| E/3.. | 1.62 | 1.59 | 1.62 | 1.53 | 1.48 | 1.70 | 1.68 | 1.51 | 1.58 |
| E/4.. | 1.64 | 1.64 | 1.64 | 1.53 | 1.47 | | 1.71 | | 1.59 |
| F/1.. | 0.05 | 0.05 | 0.06 | 0.02 | 0.05 | | 0.03 | | |
| F/2.. | 0.55 | 0.55 | 0.55 | 0.52 | | | 0.48 | | |
| F/3.. | 1.05 | 1.06 | 1.06 | 1.05 | | | 0.96 | | |
| F/4.. | 1.07 | 1.08 | 1.08 | 1.09 | | | 1.00 | | |

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LIQUORS TESTED WERE PREPARED AS FOLLOWS:

A/1, B/1, C/1, D/1, E/1, F/1—900 cc. of liquor and 100 cc. of water.

A/2, B/2, C/2, D/2, E/2, F/2—900 cc. of liquor, 50 cc. of water and 50 cc. of 10 per cent. acetic acid solution, to increase acidity one-half of 1 per cent.

A/3, B/3, C/4, D/3, E/3, F/3—900 cc. of liquor and 100 cc. of 10 per cent. acetic acid solution, to increase acidity 1 per cent.

A/4, B/4, C/4, D/4, E/4, F/4—900 cc. of liquor, 50 cc. of 10 per cent. acetic acid solution and 50 cc. of 10 per cent. lactic acid solution, figured as acetic, to increase acidity 1 per cent.

## COMMENTS.

In experience with the lime water method it was found an increase in the dilution made the determination of the end point more difficult. With the liquor made from chestnut oak extract, (D/1, D/2, D/3, D/4,) it was impossible to determine when a precipitate was formed. This liquor was very dark colored and a precipitate could not be seen. Largely diluted with water it was possible to get a result but not one that could be considered very reliable.

With calcium sucrate only 10 cc. of liquor were used which required but a few cc. of the calcium sucrate solution to neutralize. The small amount of both used made possible a greater error and if a larger amount of liquor were used doubtless the results would be more accurate.

With the gelatine precipitation method, Small's (3), the results, with the exception of those on liquor C, are lower than by any other method.

The improved quinine method was found to be troublesome and the end point difficult to determine.

The results with the charcoal method are rather surprising as previous experience with this usually gave lower results than with other methods. This method was found unsatisfactory and discarded in our regular laboratory work some time ago. Possibly the quality of the charcoal or manner of manipulation is responsible for the unexpected results given in the table.

The alcoholic gelatine-hematein and the basic dye-hematein methods gave fairly concordant results. Experience with the methods and with the color change of the indicator is neces-

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sary and with it concordant and accurate results should be obtained.

It was found that hematein could be used in many liquors without previous treatment by simply diluting sufficiently. 25 cc. of liquor were diluted with 200, 500 or 1000 cc., as required, until a bright, light yellow solution was obtained that titrated well with hematein. This was done even with strong liquors and those giving a light yellow color, sufficiently diluted, rather than a red, titrated well.

J. H. RUSSELL.

My work has been confined mainly to the two methods proposed by Mr. Reed and to the lime water method without going into work with calcium sucrate solutions but substituting tenth normal barium hydroxide.

Table I of my results are taken up with tests on made up solutions of myrabolams, chestnut and hemlock. These in their various combinations were titrated with barium hydroxide using hematein as an indicator. In the work on hemlock liquor, portions of 100 and 25 cc. were titrated to see if the discrepancies found were due to mistaking the end point in titration, apparently they are not. The results in the main checked up pretty well with the computed results, the exception being the last mixture in each case containing a large proportion of tannin with a small proportion of acid. The actual acidity of the liquors is given finally in comparison with that by lime water. The results do not check closely.

Table II gives some results with oak tannery liquors by three methods. These check pretty well except the results by Mr. Small's method.

Table III is a series of tests on a weak handler liquor titrated with both barium and calcium hydroxides in each case. An attempt was made to prepare a strong tannin solution which should be strictly neutral by adding Ba(OH), until a large precipitate formed and then filtering. That this was not the case is apparently shown in liquor 3 Table III. If tannin is to be added, it evidently must be titrated first and a correction introduced, which is an objection to the lime water method as there is no definite tannin per cent. that is known to give perfectly

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reliable acid results. The persistent difference in results between the barium and calcium hydroxides seems to be owing to differences in reading the end point rather than in an error in the absolute strength of one of the solutions as they were both standardized against the same acid.

Table IV gives results on some stronger tannery liquors by the various methods. They do not check very well.

Perhaps full justice has not been done to Mr. Reed's method with the lemon yellow O, as I was unable to use it successfully with the strength of lemon yellow that he suggested. Worked out with a .35 per cent. solution which I do not wish to maintain is the most efficient strength, but simply the one I found most convenient, the method seems to be the most satisfactory, both from the standpoint of results and availability of any I have tried. Methyl violet gave good results in most of my work, but requires a good many trials to get a successful adjustment of violet to liquor. The alcoholic gelatin is very satisfactory, but the lemon yellow seems just as easy to work and more nearly correct in its results.

Titrations with barium and calcium hydroxides on the filtered liquors give puzzling results. Sometimes the lime seems to give the best results and at other times the barium. I do not see how either could be made reliable except as more or less conventional values are obtained.

The hematein seems to be a perfectly satisfactory indicator. It checks up closely with results using phenol phthalein on all acids except lactic and even with that fairly close results can be obtained.

TABLE I.

MYRABOLAMS LIQUOR.

Liquor contained 0.5 per cent. tannin.
Mixture of acetic and lactic acids equivalent to 0.110 N acetic.
Titration made with 0.102 N barium hydroxide.
Tests by alcoholic gelatine with hematein indicator.
All mixtures made up to 250 cc. and 50 cc. titrated.

| Cc. liquor | Cc. acid | Cc. gelatine | Required cc. BaOH | Computed cc. BaOH |
|---|---|---|---|---|
| 25 | | 5 | .6 | |
| 50 | | 10 | 1.2 | |
| 25 | 30 | 5 | 7. | 7.08 |
| 25 | 20 | 5 | 4.9 | 4.92 |
| 25 | 10 | 5 | 2.8 | 2.76 |
| 50 | 10 | 10 | 3.3 | 3.36 |

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TABLE I.—(*Continued*).

CHESTNUT WOOD LIQUOR.

Liquor contained 0.5 per cent. tannin.
Mixture of acetic and lactic acids equivalent to 0.110 N acetic.
Titration made with 0.102 N barium hydroxide.
Tests by alcoholic gelatine with hematein indicator.
All mixtures made up to 250 cc., filtered and 25 cc. titrated.

| Cc. liquor | Cc. acid | Cc. gelatine | Required cc. BaOH | Computed cc. BaOH |
|---|---|---|---|---|
| 100 | | 20 | 1.8 | |
| 25 | 25 | 5 | 5.8 | 5.82 |
| 50 | 10 | 10 | 3.2 | 3.02 |
| 100 | 10 | 15 | 4.0 | 3.86 |

TESTS BY LEMON YELLOW O.

Solution Lemon Yellow O 0.35 per cent.

| | | Cc. lemon yellow | | |
|---|---|---|---|---|
| 100 | | 5 | 1.80 | |
| 25 | 25 | 5 | 5.8 | 5.85 |
| 50 | 10 | 5 | 3.3 | 3.06 |
| 100 | 10 | 5 | 4.5 | 3.96 |

TESTS BY METHYL VIOLET.

Solution Methyl Violet, 0.35 per cent.

| | | | | |
|---|---|---|---|---|
| 100 | | 2 | 1.8 | |
| 25 | 25 | 1 | 5.8 | 5.85 |
| 50 | 10 | 1 | 3.1 | 3.02 |
| 100 | 10 | 1 | 4.4 | 3.96 |

HEMLOCK LIQUOR.

Liquor contained 0.5 per cent. tannin.
Mixture of acetic and lactic acids equivalent to 0.110 N acetic.
Titrations made with 0.102 N barium hydroxide.
All mixtures made up to 250 cc. portions of 100 and 25 cc. titrated.
Tests by alcoholic gelatine method.

| Cc. liquor | Cc. acid | Cc. gelatine | BaOH required for 100 cc. | $Ba(OH)_2$ computed for 100 cc. | $Ba(OH)_2$ required for 25 cc. | $Ba(OH)_2$ computed for 25 cc. |
|---|---|---|---|---|---|---|
| 100 | | 20 | 1.4 | | .35 | |
| 25 | 25 | 10 | 10.9 | 11.1 | 2.6 | 2.78 |
| 50 | 10 | 10 | 4.8 | 5.02 | 1.2 | 1.25 |
| 100 | 10 | 15 | 5.6 | 5.72 | 1.4 | 1.43 |

TESTS BY LEMON YELLOW O METHOD.

| | | | | | | |
|---|---|---|---|---|---|---|
| 100 | | 5 | 1.9 | | .55 | |
| 25 | 25 | 3 | 11.1 | 11.3 | 2.8 | 2.84 |
| 50 | 10 | 2 | 5.2 | 5.26 | 1.3 | 1.35 |
| 100 | 10 | 5 | 5.3 | 6.22 | 1.50 | 1.63 |

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TABLE I.—(*Continued*).

TESTS BY METHYL VIOLET METHOD.

Solution of Methyl Violet.

| | | | | | | |
|---|---|---|---|---|---|---|
| 100 | | 5 | 1.8 | | 0.5 | |
| 25 | 25 | 3 | 11.2 | 11.25 | 2.65 | 2.84 |
| 50 | 10 | 3 | 5. | 5.22 | 1.25 | 1.35 |
| 50 | 50 | 5 | 21.9 | 21.50 | 5.4 | 5.65 |

Acidity of liquors computed from above tests, compared with acidity by titrating 100 cc. of filtered liquor with lime water 1 cc. equal .0027 gr. acetic acid.

| | Myrabolams | Chestnut | Hemlock |
|---|---|---|---|
| Acidity by alcoholic gelatine..... | .073 | 0.052 | 0.021 |
| " " lemon yellow..... | | .051 | .033 |
| " " methyl violet ..... | | .051 | .031 |
| " " lime water..... | .092 | .067 | .086 |

TABLE II.

OAK TANNERY LIQUORS.

No. 1. Liquor contained 0.55 per cent. tannin.

No. 2. Liquor contained 5.06 per cent. tannin.

No. 3. Liquor made from No. 2 by adding known quantity of acid results calculated to acidity of No. 2 liquor.

TESTS BY ALCOHOLIC GELATINE.

Made up to 250 cc.

| | No. cc. liquor | No. cc. gelatine | No. cc. titrated with .102 N $Ba(OH)_2$ | Per cent. acetic acid |
|---|---|---|---|---|
| 1 | 25 | 5 | 50 | 0.43 |
| 2 | 25 | 50 | 25 | .34 |
| 3 | 25 tan 25 acid | 60 | 25 | .269 |

TESTS BY LEMON YELLOW O, 0.35 PER CENT. SOLUTION.

| | | | | |
|---|---|---|---|---|
| 1 | 25 | 5 | 50 | .43 |
| 2 | 25 | 15 | 25 | .367 |
| 3 | 25 tan 25 acid | 15 | 25 | .33 |

TESTS BY METHYL VIOLET, 0.35 PER CENT. SOLUTION.

| | | | | |
|---|---|---|---|---|
| 1 | 25 | 5 | 50 | .43 |
| 2 | 25 | 15 | 25 | .368 |
| 3 | 25 tan wt. acid | 15 | 25 | .288 |

TESTS BY MR. SMALL'S WATER SOLUTION OF GELATINE.

| | | | | |
|---|---|---|---|---|
| 1 | 65 | 5 | 50 | .427 |
| 2 | 30 | 40 | 50 | .27 |
| 3 | 30 10 acid | 30 | 50 | .27 |

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TABLE III.

VARIOUS COMBINATIONS WITH A WEAK OAK HANDLER LIQUOR.

Handler liquor contained .30 per cent. tannin.

Tannin solution made from pure tannic acid. About 5 per cent. strength.

Barium hydroxide added until definite precipitate formed, solution well shaken, allowed to stand and filtered.

Acid solution made from lactic and acetic acids equivalent to 0.110 N acetic.

Barium hydroxide used in titrating 0.102 N.

Calcium hydroxide used in titrating, 1 cc. titrates 0.0027 gr. acetic acid.

All results calculated to acidity of original handler liquor.

*No. 1. Original Liquor.*

| | Per cent. acid as acetic |
|---|---|
| 10 cc. titrated after filtration with $Ba(OH)_2$ | .288 |
| 10 " " " " " $Ca(OH)_2$ | .291 |
| 25 " with 2 cc. alcoholic gelatine made up to 250 cc. | |
| 25 cc. titrated with $Ba(OH)_2$ | .245 |
| 25 cc of same titrated with lime water | .276 |
| 25 cc. with 5 cc. 0.35 per cent. lemon yellow made up to 250 cc. | |
| 25 cc. titrated with $Ba(OH)_2$ | .269 |
| 25 cc. of same titrated with $Ca(OH)_2$ | .291 |

*No. 2. 150 cc. Original Liquor, 50 cc. of 5 per cent. tannin solution.*

| | |
|---|---|
| 10 cc. filtered and titrated with $Ba(OH)_2$ | .265 |
| 10 " " " " " $Ca(OH)_2$ | .302 |
| 25 cc. with 5 cc. alcoholic gelatine made up to 250 cc. | |
| 25 cc. titrated with $Ba(OH)_2$ | .261 |
| 25 cc. of same titrated with $Ca(OH)_2$ | .296 |
| 25 cc. with 5 cc. 0.35 per cent. lemon yellow made up to 250 cc. | |
| 25 cc. titrated with $Ba(OH)_2$ | .293 |
| 25 cc. of same titrated with $Ca(OH)_2$ | .317 |

*No. 3. 100 cc. Original Liquor, 100 cc. 5 per cent. tannin solution.*

| | |
|---|---|
| 10 cc. filtered and titrated with $Ba(OH)_2$ | .275 |
| 10 cc. " " " " $Ca(OH)_2$ | .329 |
| 25 cc. with 5 cc. alcoholic gelatine made up to 250 cc. | |
| 25 cc. titrated with $Ba(OH)_2$ | .318 |
| 25 cc. of same titrated with $Ca(OH)_2$ | .356 |
| 25 cc. with 5 cc. lemon yellow made up to 250 cc. | |
| 25 cc. titrated with $Ba(OH)_2$ | .367 |
| 25 cc. of same titrated with $Ca(OH)_2$ | .432 |

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TABLE IV.

COMBINATIONS WITH A WEAK OAK HANDLER LIQUOR CONTINUED.

*No. 4. 110 cc. Original Liquor, 50 cc. Acid, 40 cc. 5 per cent. tannin liquor.*

10 cc. filtered and titrated with $Ba(OH)_2$ ..... .256
10 cc. " " " " $Ca(OH)_2$ ..... .374
25 cc. with 5 cc. alcoholic gelatine made up to 250 cc.
25 cc. titrated with $Ba(OH)_2$..... .300
25 cc. of same titrated with $Ca(OH)_2$..... 3.28
25 cc. with 5 cc. 0.35 per cent. lemon yellow made up to 250 cc.
25 cc. titrated with $Ba(OH)_2$..... .344
25 cc. of same titrated with $Ca(OH)_2$..... .330

OAK TANNERY LIQUORS BY VARIOUS METHODS.

*No. 1. Liquor contained 2.61 per cent. tannin.*

60 cc. liquor 10 cc. 2 per cent. gelatine, 50 cc. titrated with BaOH .585
10 cc. original liquor titrated with $Ba(OH)_2$ after filtering .... .55
10 cc. " " " " $Ca(OH)_2$ " " .... .751
25 cc. with 5 cc. 0.35 per cent. lemon yellow made up to 250 cc.
25 cc. titrated with $Ba(OH)_2$..... .758
25 cc. of same titrated with $Ca(OH)_2$..... .767

*No. 2. Liquor contained 4.14 per cent. tannin.*

40 cc. liquor 30 cc. 2 per cent. gelatine, 50 cc. with $Ba(OH)_2$... .539
10 cc. liquor with $Ba(OH)_2$ ..... .281
10 cc. with $Ca(OH)_2$ ..... .704
25 cc. with 10 cc. 0.35 per cent. lemon yellow made up to 250 cc.
25 cc. titrated with $Ba(OH)_2$..... .673
25 cc. titrated with $Ca(OH)_2$..... .712

*No. 3. Liquor contained 1.46 per cent. tannin.*

10 cc. titrated with $Ba(OH)_2$..... .709
10 " " " $Ca(OH)_2$..... .799
25 cc. with 5 cc. 0.35 per cent. lemon yellow made up to 250 cc.
25 cc. titrated with $Ba(OH)_2$..... .709
25 " " " $Ca(OH)_2$..... .777

## CHAS. EACHUS.

COMMENTS.

In regard to acid method would say that the charcoal method gives high results, but for sour liquors it is a satisfactory method. The quinine method is no improvement over charcoal, because the end point is indistinct. The lime water method according to Procter and Bennett is a fairly good method for an individual, but I think different chemists will get widely varying results with it. The yellow dye method will not work on all liquors and as the reaction which takes place is not very well defined, I would not be in favor of it. The gelatine hematein

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method gives very close duplicates and in my tests it gave uniform results on liquors containing vegetable acids, but with sulphuric acid liquors the acid is inversely proportional to the amount of gelatine used.

I think the gelatine hematein method would be a very good laboratory method, if the Association is satisfied that the low results that it gives are correct. Of course all of these methods determine total acid which includes non-plumping acids, as is shown in the results upon the 30° liquor made from pure chestnut wood extract. I think that either the charcoal, or gelatine methods are good laboratory methods and the choice must be made between these two. I prefer the gelatine hematein method.

| Method | 30° liquor made from chestnut wood extract in laboratory | Sole leather head liquor, 30° quebracho and chestnut wood, sulphite and sulphuric acid | 14° sole leather liquor, quebracho and chestnut wood, sulphite and sulphuric acid | 30° hemlock liquor for sole leather, vegetable acid | 25° sour hemlock liquor for sole leather, vegetable acid | 11° weak hemlock liquor for sole leather, vegetable acid | 40° new oak liquor for sole leather, vegetable acid | 30° sour oak liquor for sole leather, vegetable acid | 14° tail oak liquor for sole leather, vegetable acid | 20° new upper leather liquor, hemlock, quebracho and chestnut, vegetable acid | 10° sap upper leather liquor, hemlock, quebracho and chestnut, vegetable acid | 25° new upper leather liquor, pure quebracho, vegetable acid | 11° sap upper leather liquor, pure quebracho, vegetable acid | 26° new liquor for upper leather, quebracho, chestnut wood, sulphuric acid | 16° sap liquor for upper leather, quebracho, chestnut wood, sulphuric acid |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Charcoal... | .50 | .51 | .17 | .54 | .55 | .37 | .58 | .43 | .10 | .19 | .12 | .25 | .05 | .31 | .09 |
| Quinine.... | .34 | .35 | .41 | .46 | .50 | .45 | .50 | .47 | .22 | .19 | | .24 | .12 | | |
| Lime water | .40 | .41 | .18 | .44 | .60 | .33 | .54 | .37 | .10 | .11 | .10 | | | | |
| Gelatine-hematein | .32 | .35 | .14 | .42 | .54 | .28 | .48 | .31 | .07 | .06 | .05 | .20 | .03 | .09 | .03 |
| Yellow dye | .35 | .34 | .07 | .45 | .58 | .30 | .56 | .36 | .04 | .17 | .08 | .22 | .02 | .11 | .06 |

J. V. R. EVANS.

There is no doubt that the charcoal method is unreliable. Some of the other methods are the same. With the two gelatine methods suggested, the alcoholic solution no doubt gives the best results, but the amount of gelatine added to the liquor has an effect on the acid value obtained, the more gelatine added the lower the acid.

The quinine method will not work always, partly due to the lack of a good indicator. To me, the basic dye method is the

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best and most practical so far suggested. In working with lime water, I use a 2 oz. panel bottle, holding it at an angle of about 45° and looking through it at reading matter.

The basic dye appears to be good, you use a large amount of liquor for the determination, and with some experience on the part of the operator, good results can be obtained.

UNION LIQUORS OF VARIOUS STRENGTHS.

| | Alcoholic gelatine-hematein | | | | |
|---|---|---|---|---|---|
| Charcoal (cold) | 30 cc. liquor 30 cc. gelatine diluted to 250 | 30 cc. liquor 50 cc. gelatine diluted to 250 | 30 cc. liquor 90 cc. gelatine diluted to 250 | Quinine | Lime |
| .42 | .55 | .51 | .43 | .77 | .79 |
| .39 | .54 | .44 | .38 | .62 | |
| .36 | .45 | .36 | .32 | .66 | |
| .30 | .39 | .34 | .31 | .60 | |
| .33 | .39 | .35 | .31 | .62 | |
| .27 | .37 | .37 | .24 | .57 | .59 |
| .42 | .54 | | | | .58 |
| .61 | .63 | | | | .70 |
| .57 | .61 | | | | .73 |
| .52 | .60 | | | | .65 |
| .46 | .54 | | | | .60 |
| .41 | .60 | | | | .47 |
| | OAK LIQUORS OF VARIOUS STRENGTHS. | | | | |
| 1.08 | .93 | | | | .98 |
| 1.08 | .99 | | | | 1.14 |
| 1.10 | 1.05 | | | | 1.22 |
| .99 | .97 | | | | 1.10 |
| .83 | .82 | | | | .86 |
| .70 | .81 | | | | .91 |
| .74 | .85 | | | | .91 |
| .31 | .22 | | | | .32 |
| .81 | .73 | | | | .72 |
| .87 | .81 | | | | .85 |
| .92 | .96 | | | | 1.10 |
| .91 | .91 | | | | .97 |
| .79 | .64 | | | | .74 |
| .78 | .69 | | | | .82 |
| .87 | .84 | | | | .63 |

F. H. SMALL.

Nothing was done with either the charcoal or the quinine methods, as I had previously demonstrated to my own satisfaction that neither one is practicable for the class of liquors with which I have to deal.

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The lime method, as described, yields variable results according to the shape of the beaker used for titrating,—that is according to the depth of the liquor through which the printed paper is observed. In the case of a liquor of so deep color that printed paper cannot be seen through the same, results are affected by the degree of dilution.

As regards the basic dye method, I find the methyl-violet fails entirely with the liquors used here. No precipitate seems to be formed and the solution becomes of so deep a color that no end point is obtainable even when only a few drops of the methyl-violet are added. With the yellow dye a precipitate is formed and a titratable filtrate obtained. Some considerable practice seems necessary to properly proportion the amount of dye to liquor.

The alcoholic gelatine method seems promising and I have been able to get very good results with it. I see little advantage in either of these methods, however, over the one I am using regularly. It may be that the alcoholic gelatine method will show some advantage in ease of manipulation and speed of titration.

The following are specimen results so far obtained:—

| Liquor | A | B | C | D | E | F |
|---|---|---|---|---|---|---|
| Gelatine precip..... | .28 | .44 | .37 | .37 | .41 | .37 |
| Alcoholic gelatine ..... | .32 | .40 | .34 | .33 | .33 | .33 |
| Yellow basic dye ..... | .32 | .45 | .49 | .47 | .43 | .36 |
| Lime water ..... | .42 | .56 | .59 | | | |

A member of this Committee, J. W. Phelan, together with P. S. Fiske has published a method (the JOURNAL, April, 1908, page 99) based upon determining the amount of carbon dioxide evolved upon boiling a certain amount of liquor with calcium carbonate. According to their own figures this method is not accurate and I doubt it being any improvement over those in general use.

H. C. Reed, also a member of this Committee, has devised the alcoholic gelatine and basic dye methods, in which hematein is used as an indicator (this JOURNAL, March, 1908, page 85).

I have had a large number of tests made with the lime method on different sorts of liquors. This method has an advantage over some others in that a relatively large amount (10 cc.) of liquor is used and that, under these conditions, 1 cc. of lime

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water solution is equivalent to only about .025 per cent. of acetic acid. Ordinarily from 8 to 30 cc. of lime solution will be used.

It works better with some liquors than with others, hemlock being probably the most satisfactory. The method is very tedious and trying to carry out if a large number of tests are to be made. It is difficult to work with some dark liquors and also with those very weak in tannin. Some spent liquors will not give any definite end point and the addition of tannin does not seem to work well. Upon its addition to some liquors giving a definite precipitate, the amount of lime solution required is materially decreased. Also in a few cases the addition of tannin to liquors not giving a satisfactory end point caused a precipitate to form upon the addition of a small amount of lime solution, although these liquors showed considerable acidity by other methods. In one case the addition of tannin alone caused a precipitate. In my opinion, speaking generally, it appears to be better than either the charcoal or quinine methods. Following are some of the results of duplicate tests, expressed in number of cc. of lime water:—

| | |
|---|---|
| 12.3—12.8 | 20.4—18.9 |
| 9.8— 9.9 | 10.7—10.5 |
| 5.8— 5.9 | 4.1— 3.9 |
| 22.4—21.9 | 33.0—32.0 |
| 22.1—23.0 | 27.0—27.0 |
| 22.6—22.1 | 26.4—26.0 |
| 9.1— 9.1 | 22.4—22.3 |
| 11.3—11.2 | 12.9—12.8 |
| 13.5—13.6 | 28.1—28.2, etc. |

The quinine method has been given a thorough trial, involving tests on hundreds of samples of liquor. I do not believe it a satisfactory method for general use. In some cases it works well and gives apparently accurate results, but in others, such is not the case. One great difficulty with it is the unsatisfactory character of the end point when titrating, in some kinds of liquors this being little more than a guess. A large number of indicators have been tried, but none found that are even as satisfactory as Phenolphthalein.

The charcoal method has been given up in a number of laboratories. It is impossible to obtain a uniform charcoal which

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leads to a variety of results being obtained. As the absorption of acid by the charcoal is dependent somewhat upon the amount of tannin present in the liquors, it is very difficult to obtain a correction factor of much value. In addition, the titration in some instances, is almost as difficult as in the case with the quinine method.

The basic dye method seems to be worth further investigation. When lemon yellow O is used some liquors give filtrates that can be titrated well, and others do not. The results with the first class seem more nearly correct than the other methods. I have not been able to get satisfactory results with methyl violet.

Following are some tests on the same samples with the lime, alcoholic gelatine and basic dye (lemon yellow O) methods:—

| Lime | Gelatine | Dye |
|---|---|---|
| .79 | .74 | .72 |
| .68 | .63 | .65 |
| .30 | .24 | .24 |
| .48 | .45 | .47 |
| .42 | .42 | .54 |
| .65 | | .66 |
| .73 | | .70 |
| .70 | | .67 |
| .42 | | .36 |
| .62 | | .60 |
| .44 | | .41 |

Following are some of the results with the alcoholic gelatine method on the same samples by three persons, two of whom had no experience titrating with hematein before making these tests:—

| | Per cent. acidity | | |
|---|---|---|---|
| Sample No. 1 | .29 | .30 | .28 |
| Sample No. 2 | .44 | .43 | .41 |
| Sample No. 3 | .60 | .61 | .60 |
| Sample No. 4 | .45 | .48 | .45 |
| Sample No. 5 | .25 | .25 | .26 |
| Sample No. 6 | .36 | .35 | .36 |
| Sample No. 7 | .58 | .64 | .59 |
| Sample No. 8 | .60 | .60 | .61 |
| Sample No. 9 | .73 | .73 | .72 |
| 10 cc. of weak liquor titrated, without ppt | .06 | .06 | .06 |
| Same liquor, after ppt | .07 | .06 | .06 |
| Another sample, before ppt | .36 | .36 | .36 |
| Same sample, after ppt | .36 | .37 | .36 |

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Thirteen liquors were tested, showing acidity ranging from .52 per cent. to 1.03 per cent., the average being .84 per cent. Equal amounts of these liquors were mixed and the acid determined, two tests being made in duplicate. The results—.84, .84, .84 and .84 per cent.

OAK LIQUOR—38° Barkometer.

| | Acidity |
|---|---|
| 25 cc. liquor + 55 cc. gelatine + 175 cc. water + kaolin..... | .72 |
| 25 cc. liquor + 175 cc. water + 50 cc. gelatine + kaolin..... | .69 |
| 25 cc. liquor + 100 cc. gelatine + 125 cc. water + kaolin..... | .66 |
| 25 cc. liquor + 125 cc. water + 100 cc. gelatine + kaolin..... | .66 |
| 25 cc. liquor + 50 cc. gelatine + 425 cc. water + kaolin..... | .74 |
| 25 cc. liquor + 425 cc. water + 50 cc. gelatine + kaolin..... | .71 |
| 25 cc. liquor + 100 cc. gelatine + 375 cc. water + kaolin..... | .66 |
| 25 cc. liquor + 375 cc. water + 100 cc. gelatine + kaolin..... | .66 |
| 25 cc. liquor + 50 cc. gelatine + 925 cc. water + kaolin..... | .73 |
| 25 cc. liquor + 925 cc. water + 50 cc. gelatine + kaolin..... | .70 |
| 25 cc. liquor + 100 cc. gelatine + 875 cc. water + kaolin..... | .66 |
| 25 cc. liquor + 875 cc. water + 100 cc. gelatine + kaolin..... | .66 |

OAK LIQUOR. 40° Barkometer. 4.00 Per Cent. Tannin.

| | Acidity, per cent. | Theoretical taking 1.07 as basis |
|---|---|---|
| 25 cc. liquor + 50 cc. gelatine diluted to 250 cc., and kaolin added..... | 1.07 | |
| 50 cc. liquor + 12.5 cc. water. 25 cc. of this solution used + 50 cc. gelatine, diluted to 250 cc. and kaolin added..... | .85 | .856 |
| 50 cc. liquor + 25 cc. water. 25 cc. of this solution used + 50 cc. gelatine, diluted to 250 cc. and kaolin added..... | .71 | .713 |
| 50 cc. liquor + 50 cc. water. 25 cc. of this solution used + 50 cc. gelatine, diluted to 250 cc., and kaolin added..... | .53 | .535 |

No. 1 using 100 cc. gelatine instead of 50 cc. gave 1.04 per cent.
No. 2 using 100 cc. gelatine instead of 50 cc. gave .83 per cent.

This method has been tried on several thousand samples of liquor, and I believe it to be the best method for control work. It is easy of manipulation, rapid and with but very few exceptions all liquors that I have to test, titrate well.

It is true that different amounts of gelatine will cause some difference in results, and that this is more marked with some kinds of liquors than others, and moreso with liquors strong in tannin than in weak ones. It is only the strong liquors that the

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difference is of any material consequence. Weak liquors may be titrated, after dilution, without adding any gelatine, and the results are practically the same as those after precipitation.

Apparently the Hematein is little affected by tannin, and it is immaterial whether it is all removed or not.

The chairman would suggest that further work be done before a method for the Association is decided upon, but believe that the present "Official" charcoal method should be eliminated.

## CURRENT ARTICLES

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*Der Gerber.*

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THE ANALYSIS OF OAK WOOD EXTRACT ACCORDING TO THE NEW METHOD. *J. Jedlicka,* Aug. 29, Sept. 5.

THE CHEMISTRY OF CHROME TANNING. *E. Stiasny,* Sept. 5.

A DELICATE COLLOID REACTION FOR SOME METALLIC SALTS. *E. Stiasny,* Sept. 5, 12.

SECOND REPORT, INTERNATL. COMMISSION ON TANNIN ANALYSIS. *H. R. Procter,* Sept. 12.

ESTIMATION OF FREE SULPHURIC ACID IN LEATHER. *Drs. Paessler* and *Arnoldi,* Sept. 12.

DE-HAIRING WITH SUPHUROUS ACID. *U. J. Thuau,* (in French), Sept. 12.

ESTIMATION OF NON-TANNINS. *H. R. Zeuthen,* Sept. 12.

A RAPID METHOD FOR DETERMINATION OF SOLUBLE HIDE SUBSTANCE IN SOAKS AND LIMES. *E. Stiasny,* Sept. 12, 19.

THE TANNINS OF NEW CALEDONIA. *U. J. Thuau,* (in French), Sept. 19.

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AN IMPROVED FAT LIQUOR FOR CHROME AND STRAIGHT TANNED LEATHER. Sept. 9.

THE TANNING BARKS OF QUEENSLAND. Sept. 9.

THE SUMAC MARKET. Oct. 7.

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# REVIEWS.

**The Use of the Zeiss Immersion Refractometers for Tannin Analysis.** KARL G. ZWICK. *Gerber Zeitung*, 1908 [51], Nos. 154, 157, 160, 161, 164, 170, 171, 174.—In our present ignorance of the chemical constitution of the tan-stuffs, no method of analysis is likely to supplant the hide-powder methods which approximate conditions obtaining in direct tanning and may be expected to give the most useful results for practice. The method here described is intended to supplement the hide-powder absorption by direct examination of the filtrates, avoiding the tedious evaporations and weighings. This has already been attempted by observation of specific gravities with hitherto unsatisfactory results. The principle of the author's method in brief, is to measure the optical refraction of the tan solution, before and after absorption with hide-powder, the diminution being proportional to tan contents. In the instrument employed, a prism terminating a vertical observing tube is immersed in the liquid contained in a small tube and the boundary line of the total reflection (by direct daylight) read off on an arbitrary scale in the eye-piece. This reading is used directly conversion into the refractive index being here unnecessary. As the refraction varies greatly with the temperature, the instrument is provided with a bath which maintains a constant temperature. 17.5°C being normal (corrections can be made for other temperatures). The normal adjustment for pure water at 17.5° requires a reading of 15. If for instance the scale readings (corrected) for a solution before and after de-tanning are 17.50 and 15.56, then the scale intervals are 2.5 for total solubles, 0.56 for non-tans and 1.94 for tans.

An extensive series of experiments were made with tan solutions of official strengths which were also analyzed by the usual methods. The percentage of tans determined gravimetrically was compared with the difference in refractometer readings before and after de-tanning. It was found that these scale differences were proportional to the tans absorbed, although different ratios were found for different tanning materials. The highest results gave 1 scale division=0.2% tans and the instrument itself can be read with an accuracy of 1/10 division, giving a probable error of .02%. With extracts diluted 100-200 times the error is correspondingly multiplied. Extracts from the author's tables follow:

TABLE I.

*Liquors, Vat Series A.*

| | Refractometer scale reading | | | Per cent. tans | | Per cent. non-tans | |
|---|---|---|---|---|---|---|---|
| | before detanning | after detanning | diff. | refractometer method | shake method | refractometer method | shake method |
| Vat 1, dilute ¼ | 5.45 | 3.70 | 1.75 | .336 | .337 | .691 | .724 |
| " 2 " 1/5 | 5.27 | 3.31 | 1.96 | .376 | .383 | .619 | .644 |
| " 3 " " | 5.00 | 3.25 | 1.75 | .336 | .342 | .607 | .640 |
| " 4 " " | 5.39 | 3.28 | 2.11 | .405 | .423 | .613 | .646 |
| " 5 " " | 5.67 | 3.29 | 2.38 | .457 | .469 | .615 | .624 |
| " 6 " " | 6.06 | 3.28 | 2.78 | .533 | .519 | .613 | .649 |
| " 7 " " | 5.96 | 3.22 | 2.74 | .526 | .522 | .602 | .582 |
| " 8 " " | 6.98 | 3.48 | 3.50 | .672 | .645 | .650 | .643 |

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TABLE II.

*Liquors, Vat Series B.*

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Vat 1, dilute ¼ | 4.75 | 3.42 | 1.33 | .246 | .248 | .658 | .698 |
| " 2 " " | 6.14 | 4.05 | 2.09 | .387 | .406 | .786 | .776 |
| " 3 " 1/5 | 4.88 | 2.91 | 1.97 | .364 | .362 | .559 | .592 |
| " 4 " " | 6.04 | 3.46 | 2.58 | .477 | .460 | .665 | .646 |
| " 5 " " | 5.85 | 3.34 | 2.51 | .464 | .458 | .641 | .618 |
| " 6 " " | 6.65 | 3.54 | 3.11 | .575 | .574 | .679 | .646 |
| " 7 " 1/6.7 | 5.01 | 2.41 | 2.60 | .481 | .482 | .464 | .482 |
| " 8 " " | 5.60 | 2.64 | 2.96 | .547 | .544 | .507 | .518 |

TABLE III.

*Liquors, Vat Series C.*

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Vat 1, dilute ¼ | 5.32 | 3.30 | 2.02 | .288 | .281 | .841 | .808 |
| " 2 " " | 6.30 | 3.58 | 2.72 | .389 | .393 | .912 | .875 |
| " 3 " 1/5 | 5.89 | 2.80 | 3.09 | .442 | .437 | .714 | .725 |
| " 4 " " | 6.00 | 2.90 | 3.10 | .443 | .435 | .739 | .752 |
| " 5 " " | 6.30 | 2.89 | 3.41 | .487 | .479 | .737 | .742 |
| " 6 " " | 7.21 | 3.00 | 4.21 | .602 | .606 | .765 | .795 |
| " 7 " 1/6.7 | 5.48 | 2.22 | 3.26 | .466 | .469 | .566 | .584 |
| " 8 " " | 6.08 | 2.30 | 3.78 | .540 | .560 | .586 | .591 |

1 scale division = 0.192 per cent. tans, 0.187 per cent. non-tans, Series A.
" " " 0.185 " " " 0.192 " " " " B.
" " " 0.143 " " " 0.255 " " " " C.

This method was worked out primarily for factory control in leather or extract making and seems adapted for that purpose, being rapid, even if not so accurate as the gravimetric method for extract analysis. Moreover since the refraction depends not only on the amount but on the nature of the substances in solution, the method may often be employed to aid in determining their character, as shown in the following table of analyses of quebracho extract.

TABLE IV.

| | Shake method Per cent. tans gravim. | Shake method 1 scale division = per cent. | Filter method Per cent. tans gravim. | Filter method 1 scale division = per cent. |
|---|---|---|---|---|
| Quebracho wood, 20 gm. to lit..... | 0.337 | 0.166 | 0.350 | 0.169 |
| Solid extract I, 5 " " " ..... | 0.349 | 0.168 | 0.355 | 0.169 |
| Liquid " F, 10 " " " ..... | 0. | | 0.325 | 0.172 |
| " " C, 10 " " " ..... | 0.314 | 0.186 | 0.340 | 0.184 |
| " " S, 10 " " " ..... | 0.320 | 0.177 | 0.346 | 0.173 |

Quebracho wood and solid extract give the same scale equivalents (0.168) while extract C has an equivalent of 0.186. Myrabolams was also d

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to have a high equivalent, 0.195; hence it may be suspected that the brand C has been blended as well as S to a less extent. The quality of the leather produced confirmed this conclusion.

The tables I, II, III, show the variation in scale equivalent caused by using different materials for extraction (business interests prevent the author from revealing the composition of these liquors). The change is gradual until the final factor 0.143 is reached.

The optical investigation does not interfere with the analysis of liquors in the usual way since the solutions are not consumed. It is hoped that by further study a series of limiting values may be determined upon which one may rely in forming an opinion as to the character of the tans present, particularly in the case of adulteration or blending. It is not feasible to make a tan determination by direct refractometric examination alone since the influence of the non-tans is unknown. The determination of non-tans in this way is only reliable in special cases, as for instance in the control of a series of extractions with uniform materials, when the figures will be proportional to the concentrations. Another application has proved of value; two commercial extracts of the same designation gave the same non-tans by gravimetric analysis but the difference by optical examination was considerable and the conclusion was that the extracts were different.

To study the results with stronger solutions, measurements were made with solutions of pure tannin, observation being difficult with dark-colored extracts. The factors found were fairly constant.

| Tannin per cent. | Scale degrees refractometer | Divisions for 1 per cent. |
|---|---|---|
| 15 | 79.5 | 5.3 |
| 10 | 53.2 | 5.32 |
| 5 | 26.0 | 5.20 |
| 2 | 10.5 | 5.25 |
| 1 | 5.38 | 5.38 |

One advantage of the optical method does not show up in the figures; suspended matter not in solution has no effect and is therefore not included in the measurements.

**A New Method of Tannin Estimation.** G. METZER. *Collegium*, 1908, No. 318, pp. 259-60.—The principle consists in subjecting the solution of tanning material to the action of an alternating current through aluminum electrodes, the tans being completely precipitated, whether chemically or physically is yet uncertain. A 110 volt direct current passes through four 16-candle lamps in parallel and a rotary converter operated by a small turbine or motor. The solution, prepared according to the official method is placed in an aluminum dish and an aluminum plate forms the other

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electrode. The separation is complete in 30 minutes which may be verified by a ferric salt or gelatine test. The precipitate is filtered off and 50 cc. of the filtrate used for determination of non-tans in the usual way. Results have been obtained agreeing well with those by hide-powder. The author expects to make extended comparative analyses and publish later.

**The Determination of the Solubilities of Tanning Extracts.** J. PAESSLER AND TH. VEIT. *Collegium*, 1908, Nos. 322-4, pp. 295-304, 308-20, 322-31.—In general the results of the determination of insolubles by the usual analytical process do not apply to the preparation of strong liquors. The analysis is carried out in very weak solutions, 0.2-0.4°B, giving little insoluble. In the preparation of strong liquors for tanning, considerable amounts of difficultly soluble tans, generally separate. In this respect however extracts vary greatly, some giving little sediment. The value of an extract in general will be so much the greater, the clearer the liquors and the usual extract analysis takes no account of this.

*Method of Determination of Solubilities.*—Amounts of the extract are dissolved which according to the analysis contain:

| | | | | |
|---|---|---|---|---|
| Total solubles, gms..... | 5 | 12.5 | 25 | 35.5 |
| Strength No..... | 1 | 2 | 3 | 4 |

These solutions are made up to 250 cc. in two ways, (a), 2 hours shaking in a flask with nearly 250 cc. water at ordinary temperature, afterwards filling to the mark; (b) by solution at 90-100° in water, total volume 250 cc., then slow cooling, leaving stand and finally filling to the mark. The solutions are filtered, specific gravity taken, and the total solubles determined. An amount of each solution is taken for evaporation corresponding to 1 gm. total solubles in the original extract by analysis, therefore 50, 20, 10 and 6.7 cc. for the strengths 1, 2, 3, 4. The entire analysis should be carried out in one day to avoid errors from separation of difficultly soluble tans.

From the weights of the residues by evaporation the total solubles (recovered) are computed in percentage of the original extract, and also in percentage of the original total solubles as found by analysis. Since the sediment separating from strong liquors contains difficultly soluble tans only and the non-tans remain in solution, it is better to compute the utilization based on tans only. The non-tans therefore (as found by analysis) are deducted from the total solubles found in the solubility experiments, leaving soluble tans which are compared with the tans determined by analysis. We give the author's first table in full and give the essential empirical data in the remaining 24 tables with the final results; the filter-method data are entirely omitted, the differences little affecting the utilization ratios.

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*TABLE I. Oakwood Extract No. 1.*

Analysis (shake method)

Tans ..... 22.2
Non-tans .... 18.0
Total solubles 40.2
Insoluble .... 0.3

| | Dissolved cold Strengths | | | | Dissolved hot Strengths | | | |
|---|---|---|---|---|---|---|---|---|
| | 1 | 2 | 3 | 4 | 1 | 2 | 3 | 4 |
| Gms. extr. taken .. | 12.44 | 31.09 | 62.19 | 93.28 | 12.44 | 31.09 | 62.19 | 93.28 |
| Spec. grav. filtrate .. | 1.0078 | 1.018 | 1.0375 | 1.060 | 1.0075 | 1.018 | 1.0405 | 1.060 |
| Same, barkometer . | 7.8 | 18.0 | 37.5 | 60.0 | 7.5 | 18.0 | 40.5 | 60.0 |
| Same, Baumé | 1.15 | 2.60 | 5.30 | 8.30 | 1.10 | 2.60 | 5.70 | 8.30 |
| Gms. evap. residue .. | .9250 | .9100 | .8950 | .9053 | .9450 | .9370 | .9265 | .9250 |
| Total solubles, per cent ..... | 37.2 | 36.6 | 36.0 | 36.4 | 38.0 | 37.7 | 37.3 | 37.2 |
| Non-tans. per cent. | 18.0 | 18.0 | 18.0 | 18.0 | 18.0 | 18.0 | 18.0 | 18.0 |
| Soluble tans. per cent. | 19.2 | 18.6 | 18.0 | 18.4 | 20.0 | 19.7 | 19.3 | 19.2 |
| Solubles utilized per cent. | 92.5 | 91.0 | 89.5 | 90.5 | 94.5 | 93.7 | 92.7 | 92.5 |
| Tans. utilized, per cent ..... | 86.5 | 83.5 | 81.1 | 82.9 | 90.1 | 88.7 | 86.9 | 86.5 |

*II. Oak Wood, 3.*

| | | | Dissolved cold | | | | Dissolved hot | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | 1 | 2 | 3 | 4 | 1 | 2 | 3 | 4 |
| Tans .... 23.6 | Grav. B° .... | | 1.10 | 2.75 | 5.5 | 8.25 | 1.15 | 2.75 | 5.5 | 7.8 |
| Non-tans. 17.1 | Soluble tans. | | 21.4 | 21.0 | 21.0 | 21.0 | 21.5 | 21.8 | 21.4 | 21.6 |
| Soluble .. 40.7 | Tans. utilized | | 90.7 | 89.0 | 89.0 | 89.0 | 91.1 | 92.4 | 90.7 | 91.5 |
| Insol .... 0.0 | | | | | | | | | | |

*III. Oakwood, 4.*

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Tans .... 22.3 | Grav. B° .... | 1.05 | 2.8 | 5.5 | 8.3 | 1.2 | 2.85 | 5.65 | 8.45 |
| Non-tans. 19.6 | Soluble tans. | 20.2 | 20.4 | 20.0 | 19.9 | 21.1 | 20.6 | 20.5 | 20.5 |
| Soluble .. 41.9 | Tans. utilized | 90.6 | 91.5 | 89.7 | 89.3 | 94.6 | 92.4 | 91.9 | 91.9 |
| Insol .... 0.2 | | | | | | | | | |

*IV. Chestnut Wood, 1.*

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Tans .... 26.3 | Grav. B° .... | 1.2 | 2.8 | 5.65 | 8.35 | 1.15 | 2.85 | 5.8 | 8.6 |
| Non-tans. 14.6 | Soluble tans. | 24.9 | 25.4 | 25.4 | 25.2 | 24.6 | 24.8 | 25.5 | 25.7 |
| Soluble .. 40.7 | Tans. utilized | 94.7 | 96.6 | 96.6 | 95.8 | 93.5 | 94.3 | 96.9 | 97.7 |
| Insol .... 0.7 | | | | | | | | | |

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| | | | Dissolved cold | | | | Dissolved hot | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | 1 | 2 | 3 | 4 | 1 | 2 | 3 | 4 |
| *V. Chestnut Wood, 2.* | | | | | | | | | | |
| Tans .... | 33.2 | Grav. B°.... | 1.05 | 2.9 | 5.75 | 8.65 | 0.95 | 2.9 | 5.7 | 8.65 |
| Non-tans. | 15.2 | Soluble tans. | 30.7 | 31.1 | 31.7 | 32.4 | 29.3 | 31.5 | 31.8 | 32.9 |
| Soluble.. | 48.4 | Tans.utilized | 92.5 | 93.7 | 95.5 | 97.6 | 88.3 | 94.6 | 95.8 | 99.1 |
| Insol .... | 1.1 | | | | | | | | | |
| *VI. Chestnut Wood, 3.* | | | | | | | | | | |
| Tans .... | 28.9 | Grav. B°.... | 1.15 | 2.95 | 5.8 | 8.7 | 1.25 | 2.95 | 5.85 | 8.9 |
| Non-tans. | 9.8 | Soluble tans. | 27.6 | 27.6 | 27.7 | 27.9 | 27.7 | 27.6 | 28.0 | 28.1 |
| Soluble.. | 38.7 | Tans.utilized | 95.5 | 95.5 | 95.9 | 96.5 | 95.9 | 95.5 | 96.9 | 97.2 |
| Insol .... | 0.2 | | | | | | | | | |
| *VII. Chestnut Wood, 4.* | | | | | | | | | | |
| Tans .... | 29.5 | Grav. B°.... | 1.15 | 2.9 | 5.7 | 8.7 | 1.15 | 2.9 | 5.85 | 8.75 |
| Non-tans. | 11.2 | Soluble tans. | 27.6 | 28.1 | 28.3 | 28.1 | 27.7 | 28.1 | 28.4 | 28.2 |
| Soluble.. | 40.7 | Tans.utilized | 93.5 | 95.3 | 95.9 | 95.3 | 94.2 | 95.3 | 96.3 | 95.6 |
| Insol .... | 0.5 | | | | | | | | | |
| *VIII.* | | | | | | | | | | |
| *Quebracho, solid, regular, 1.* | | | | | | | | | | |
| Tans .... | 62.1 | Grav. B°.... | 0.65 | 1.6 | 3.0 | 4.4 | 0.75 | 1.95 | ... | 5.05 |
| Non-tans. | 11.7 | Soluble tans. | 37.2 | 35.2 | 33.3 | 32.5 | 54.0 | 46.2 | 38.9 | 38.8 |
| Soluble.. | 73.8 | Tans.utilized | 59.9 | 56.7 | 53.6 | 52.3 | 87.0 | 74.4 | 62.6 | 62.5 |
| Insol .... | 9.0 | | | | | | | | | |
| *IX.* | | | | | | | | | | |
| *Quebracho, solid, regular, 2.* | | | | | | | | | | |
| Tans .... | 67.2 | Grav. B°.... | ... | ... | ... | ... | ... | ... | ... | ... |
| Non-tans. | 9.6 | Soluble tans. | 47.8 | 38.8 | 36.2 | 36.0 | 58.6 | 52.1 | 45.9 | 40.1 |
| Soluble.. | 76.6 | Tans.utilized | 71.1 | 57.7 | 53.9 | 53.6 | 87.2 | 77.5 | 68.3 | 59.7 |
| Insol .... | 8.1 | | | | | | | | | |
| *X. Quebracho, liquid, 3.* | | | | | | | | | | |
| Tans .... | 31.0 | Grav. B°.... | 0.7 | 1.75 | 4.0 | 6.05 | 0.75 | 2.10 | 4.30 | 6.40 |
| Non-tans. | 5.9 | Soluble tans. | 25.9 | 25.9 | 24.1 | 24.1 | 28.2 | 26.4 | 26.2 | 26.0 |
| Soluble.. | 36.9 | Tans.utilized | 83.5 | 83.5 | 77.7 | 77.7 | 91.0 | 85.2 | 84.5 | 83.9 |
| Insol .... | 2.3 | | | | | | | | | |
| *XI. Quebracho, liquid, 4.* | | | | | | | | | | |
| Tans .... | 31.4 | Grav. B°.... | 0.85 | 2.35 | 4.35 | 6.6 | 0.85 | 2.3 | 4.4 | 6.55 |
| Non-tans. | 7.3 | Soluble tans. | 28.0 | 27.0 | 26.3 | 27.4 | 26.9 | 27.3 | 26.4 | 26.7 |
| Soluble.. | 38.7 | Tans.utilized | 89.2 | 86.0 | 83.8 | 87.3 | 85.7 | 86.9 | 84.1 | 85.0 |
| Insol .... | 1.3 | | | | | | | | | |
| *XII. Quebracho, liquid, 5.* | | | | | | | | | | |
| Tans .... | 30.6 | Grav. B°.... | 0.9 | 2.4 | 4.9 | 6.9 | 1.0 | 2.2 | 4.95 | 7.0 |
| Non-tans. | 7.8 | Soluble tans. | 28.3 | 28.3 | 28.5 | 29.6 | 28.4 | 28.1 | 28.5 | 29.2 |
| Soluble | 38.4 | Tans.utilized | 92.5 | 92.5 | 93.1 | 96.4 | 92.8 | 91.8 | 93.1 | 95.2 |
| Insol .... | 0.1 | | | | | | | | | |

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| | | | Dissolved cold | | | | Dissolved hot | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | 1 | 2 | 3 | 4 | 1 | 2 | 3 | 4 |
| *XIII. Quebracho, liquid, 6.* | | | | | | | | | | |
| Tans .... 32.5 | Grav. B°.... | 1.0 | 2.45 | 4.9 | 7.5 | 1.0 | 2.45 | 4.95 | 7.5 |
| Non-tans. 7.0 | Soluble tans. | 29.0 | 30.5 | 30.7 | 32.0 | 30.5 | 31.0 | 31.2 | 32.2 |
| Soluble.. 39.5 | Tans. utilized | 89.2 | 93.8 | 94.5 | 98.5 | 93.8 | 95.4 | 96.0 | 99.1 |
| Insol .... 0.9 | | | | | | | | | |
| *XIV. Quebracho, liquid, 7.* | | | | | | | | | | |
| Tans .... 29.2 | Grav. B°.... | 1.0 | 2.65 | 5.2 | 7.9 | 1.0 | 2.65 | 5.3 | 8.0 |
| Non-tans. 8.7 | Soluble tans. | 27.9 | 28.4 | 28.1 | 29.3 | 28.7 | 28.5 | 28.6 | 29.2 |
| Soluble.. 37.9 | Tans. utilized | 95.5 | 97.3 | 96.2 | 100.0 | 98.3 | 97.6 | 97.8 | 100.0 |
| Insol .... 0.3 | | | | | | | | | |
| *XV. Quebracho, liquid, 8.* | | | | | | | | | | |
| Tans .... 33.5 | Grav. B°.... | 1.0 | 2.45 | 4.9 | 7.5 | 1.0 | 2.4 | 4.95 | 7.5 |
| Non-tans. 9.2 | Soluble tans. | 31.2 | 31.6 | 32.0 | 32.7 | 31.4 | 31.8 | 31.8 | 33.3 |
| Soluble.. 42.7 | Tans. utilized | 93.1 | 94.3 | 95.5 | 97.6 | 93.7 | 94.9 | 94.9 | 99.4 |
| Insol .... 0.8 | | | | | | | | | |
| *XVI. Quebracho, liquid, 9.* | | | | | | | | | | |
| Tans .... 29.1 | Grav. B°.... | 1.0 | 2.55 | 5.25 | 7.85 | 1.05 | 2.5 | 5.25 | 7.85 |
| Non-tans. 8.8 | Soluble tans. | 28.7 | 28.5 | 28.8 | 29.1 | 28.8 | 28.8 | 28.3 | 29.0 |
| Soluble.. 37.9 | Tans. utilized | 98.6 | 98.0 | 99.0 | 100.0 | 99.0 | 99.0 | 97.3 | 100.0 |
| Insol .... 0.0 | | | | | | | | | |
| *XVII. Quebracho, liquid, 10.* | | | | | | | | | | |
| Tans .... 30.4 | Grav. B°.... | 1.0 | 2.6 | 5.15 | 7.85 | 1.0 | 2.6 | 5.2 | 7.85 |
| Non-tans. 8.5 | Soluble tans. | 30.0 | 29.9 | 29.5 | 30.4 | 29.8 | 30.0 | 29.3 | 30.4 |
| Soluble.. 38.9 | Tans. utilized | 98.7 | 98.4 | 97.0 | 100.0 | 98.0 | 98.7 | 96.4 | 100.0 |
| Insol .... 0.0 | | | | | | | | | |
| *XVIII. Quebracho, liquid, 11.* | | | | | | | | | | |
| Tans .... 29.0 | Grav. B°.... | 1.1 | 2.45 | 5.15 | 7.85 | 1.15 | 2.3 | 5.1 | 7.8 |
| Non-tans. 6.8 | Soluble tans. | 28.9 | 29.3 | 29.3 | 30.3 | 29.4 | 29.4 | 29.6 | 30.8 |
| Soluble.. 35.8 | Tans. utilized | 99.7 | 101.1 | 101.1 | 105.0 | 101.0 | 101.0 | 102.0 | 106.0 |
| Insol .... 2.4 | | | | | | | | | |
| *XIX. Quebracho, liquid, 12.* | | | | | | | | | | |
| Tans .... 33.5 | Grav. B°.... | 1.2 | 3.2 | 6.2 | 9.3 | 1.25 | 3.25 | 6.3 | 9.35 |
| Non-tans. 15.6 | Soluble tans. | 33.9 | 33.9 | 34.0 | 34.3 | 33.4 | 33.8 | 34.9 | 34.5 |
| Soluble.. 49.1 | Tans. utilized | 101.1 | 101.1 | 101.5 | 102.3 | 100.6 | 100.9 | 104.2 | 102.9 |
| Insol .... 0.9 | | | | | | | | | |
| *XX. Pine Bark, 1.* | | | | | | | | | | |
| Tans .... 16.5 | Grav. B°.... | 0.85 | 2.3 | 4.8 | 4.8 | 0.9 | 2.35 | 4.4 | 7.4 |
| Non-tans. 23.1 | Soluble tans. | 15.7 | 14.7 | 15.0 | 15.4 | 15.6 | 15.6 | 14.7 | 15.2 |
| Soluble.. 39.6 | Tans. utilized | 95.2 | 89.1 | 90.9 | 93.3 | 94.5 | 94.5 | 89.1 | 92.1 |
| Insol .... 1.2 | | | | | | | | | |

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| | | | Dissolved cold | | | | Dissolved hot | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | 1 | 2 | 3 | 4 | 1 | 2 | 3 | 4 |
| *XXI. Pine Bark, 2.* | | | | | | | | | | |
| Tans .... | 14.2 | Grav. B°.... | .... | .... | .... | .... | .... | .... | .... | .... |
| Non-tans. | 17.4 | Soluble tans. | 11.6 | 11.1 | 11.2 | 11.4 | 12.9 | 11.2 | 10.8 | 11.0 |
| Soluble.. | 31.6 | Tans utilized | 81.7 | 78.2 | 78.9 | 80.3 | 90.9 | 78.9 | 76.8 | 77.5 |
| Insol .... | 2.5 | | | | | | | | | |
| *XXII. Mallet.* | | | | | | | | | | |
| Tans .... | 32.8 | Grav. B°.... | 1.0 | 2.5 | 5.05 | 7.55 | 1.0 | 2.6 | 5.0 | 7.5 |
| Non-tans. | 11.1 | Soluble tans. | 30.6 | 30.9 | 31.7 | 31.7 | 32.2 | 31.3 | 31.4 | 31.7 |
| Soluble.. | 43.9 | Tans utilized | 93.9 | 94.2 | 96.7 | 96.7 | 98.2 | 95.5 | 95.8 | 96.7 |
| Insol .... | 0.8 | | | | | | | | | |
| *XXIII. Mangrove.* | | | | | | | | | | |
| Tans .... | 30.6 | Grav. B°.... | 1.05 | 2.65 | 5.3 | 8.2 | 1.05 | 2.65 | 5.35 | 8.05 |
| Non-tans. | 11.3 | Soluble tans. | 30.5 | 30.6 | 31.2 | 31.7 | 30.6 | 30.9 | 31.0 | 31.3 |
| Soluble.. | 41.9 | Tans utilized | 99.6 | 100.0 | 102.0 | 103.6 | 100.0 | 101.0 | 101.3 | 102.3 |
| Insol .... | 1.4 | | | | | | | | | |
| *XXIV. Mimosa.* | | | | | | | | | | |
| Tans .... | 18.4 | Grav. B°.... | 1.1 | 2.5 | 5.25 | 7.85 | 1.0 | 2.5 | 5.15 | 7.8 |
| Non-tans. | 9.9 | Soluble tans. | 16.2 | 16.7 | 17.4 | 17.1 | 17.4 | 17.0 | 17.0 | 16.9 |
| Soluble.. | 28.3 | Tans utilized | 88.1 | 90.8 | 94.6 | 92.9 | 94.6 | 92.4 | 92.4 | 91.8 |
| Insol .... | 0.4 | | | | | | | | | |
| *XXV. Myrabolams.* | | | | | | | | | | |
| Tans .... | 18.2 | Grav. B°.... | 1.1 | 2.8 | 5.35 | 8.15 | 1.1 | 2.8 | 5.35 | 8.3 |
| Non-tans. | 16.7 | Soluble tans. | 16.0 | 15.8 | 16.2 | 17.0 | 16.4 | 15.8 | 15.8 | 16.6 |
| Soluble.. | 34.9 | Tans utilized | 87.9 | 86.8 | 89.1 | 93.4 | 90.1 | 86.8 | 86.8 | 91.2 |
| Insol .... | 3.6 | | | | | | | | | |

In judging the utilization figures, conclusions should not be based on differences of less than 1 to 2%, considering the opportunities for experimental errors. The results obtained with hot solutions are first discussed and divided into four classes; (1) the utilization decreases as the solutions become stronger; the foremost example is non-treated quebracho (difficultly soluble); (2) the utilization is nearly constant but may be subdivided into (a) nearly 100%, comprising cold soluble (chemically treated) quebracho, mangrove and many chestnut extracts, (b) below 100%, including oak-wood, mallet, mimosa, several chestnut extracts and many of treated quebracho; (3) the utilization increases with the concentration, including most chestnut and many treated quebracho extracts; the utilization decreases until the 2d or 3d strength and then increases with the concentration, including many treated quebracho and myrabolams extracts.

It is remarkable that in some cases, the difficultly soluble tans are more soluble in concentrated solutions than weak. Such extracts are economically used for concentrated liquors as for instance in drum tan-

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nage. In a few cases, the apparently paradoxical result of over 100% utilizatioin is reached; this is probably due to the difficultly soluble tans remaining among the insolubles on analysis but dissolving in the stronger solutions.

The results for solutions at ordinary temperatures do not differ in most cases from the others; in the difficultly soluble quebracho extracts they are throughout lower. The method ordinarily therefore need be employed with hot solutions. Colleagues are requested to use this method in solubility determinations.

**The Analysis of Oak Wood Extract According to the New Official Method.** J. JEDLICKA. *Collegium*, 1908, Nos. 324-5, pp. 331-6.—This is a continuation of the study of influence of chromium content (abstr. this JOURNAL, 1908, [3], No. 3, p. 95). The factory extracts (Mitrovitz) were analyzed with the same hide-powder, chromed in 6 strengths, ranging from 0.1 to 1% Cr, these being the limits latterly recommended by Dr. Procter.

| Ext. | Hide powder | Percentage of Cr in Hide Powder | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | 0 | 0.1 | 0.2 | 0.4 | 0.5 | 0.8 | 1.0 |
| I | A | 19.0 | 18.7 | 18.5 | 18.1 | 17.9 | 17.0 | 16.9 |
| II | " | 18.5 | 18.3 | 18.5 | 17.5 | 16.7 | 16.4 | 16.1 |
| III | " | 18.5 | 18.5 | 18.3 | 17.4 | 17.1 | 16.7 | 16.4 |
| IV | " | 17.1 | 17.0 | 17.0 | 16.4 | 16.2 | 15.7 | 15.2 |
| V | " | 18.3 | 18.2 | 18.0 | 17.7 | 17.6 | 16.7 | 16.5 |
| VI | " | 19.0 | 18.6 | 18.3 | 17.9 | 17.7 | 17.3 | 16.9 |
| " | " | 18.5 | 18.2 | 18.1 | 17.9 | 17.4 | 17.7 | 16.7 |
| " | " | 18.7 | 18.5 | 18.3 | 17.9 | 17.5 | 16.8 | 16.6 |
| " | " | 18.8 | 18.5 | 18.4 | 18.0 | 17.8 | 16.9 | 16.6 |
| " | B | 19.6 | 19.5 | 19.3 | 18.4 | 18.2 | 17.9 | 17.6 |
| " | " | 19.8 | 19.5 | 19.3 | 18.6 | 18.2 | 17.7 | 17.4 |
| " | " | 20.2 | 19.7 | 19.6 | 18.8 | 18.5 | 17.5 | 17.5 |
| " | " | 19.8 | 19.7 | 19.4 | 18.7 | 18.6 | 17.4 | 17.3 |

For comparison, the unchromed hide-powder was also used; this was washed until no cloudiness resulted with tannin solution. The results of the entire series showed that concordant results were obtained for any one proportion of Cr, but that the absorption increased regularly with increase of Cr giving an average difference of 1.9% non-tans for the entire range. It is therefore not a matter of indifference as to the amount of Cr which for uniformity should be prescribed within narrow limits, perhaps as close as 0.1%; in the interests of non-associates the limits 1-2% Cr would perhaps be the most suitable, the differences being less with strongly chromed hide-powder. As to which results are the most correct, there is no criterion.

The earlier work gave concordant results with hide-powder from two sources. Hide-powder (B) was a disappointment, containing 3.4% solubles yielded with one shaking, and gave over 1% higher non-tans on use; it was improved by protracted washing till it gave 0.5% higher results than (A).

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*Solubility of Chromed Hide-Powder.*—The writer has never succeeded in washing down to the prescribed limit, 5 mg. in 100 cc. but obtained results ranging from 8-15 mgs., according to temperature (the laboratory in summer is over 30°C). This causes an increase of 0.6-1.2% non-tans. Although Dr. Procter reaches 1 mg., many colleagues have also found solubles (Paessler, Zeuthen in Commission Report, 27 mg., 6-11 mg.) Authors found chlorine in filtrate but never Cr. It is recommended that in analysis the solubles in the chromed hide-powder be determined separately by blank test and deducted. The increased labor is slight and the squeezed hide-powder may be used for analysis. The solubles from 5 washings gave 21% ash which itself contained 70% soluble; this last was 85% NaCl, the insoluble part containing much Ca and traces of Fe.

The cause of the decrease in non-tans with increase in Cr is attributed to the presence of a greenish-yellow dye-stuff in oakwood, which does not precipitate gelatine and is adjective towards cotton (that is, dyes only with mordants). It is taken up by hide with more difficulty than tans. In the filter method when the upper part of the hide-powder is still intact, the dye-stuff is absorbed, giving colorless solutions. Wtih the shake method, the filtrates are more yellow, according to the amount of Cr; with 5% $Cr_2O_3$ colorless filtrates are sometimes obtained. Also by re-treating with additional hide-powder, the yellow solutions are decolorized. The dye-stuff leaches out of wood with difficulty and therefore is principally found in the last members of the diffusion battery. This dye-stuff is probably analogous to quercitrin, and is being investigated as free time offers. It would be premature to classify this body with the non-tans as useless because of its slow absorption in comparison with the tan-stuffs.

**Determination of Free Sulphuric Acid in Leather by the Aid of Electric Ignition and Cobalt Oxide as an Oxygen Carrier.** J. PAESSLER and DR. ARNOLDI. *Collegium,* 1908, No. 326, pp. 358-61.—This method was devised to avoid the errors resulting from overheating in Balland and Maljean's original process or the too violent oxidation taking place in Meunier's modification (in presence of free alkali and saltpetre). In order to operate at a moderate temperature, Schopper's electric ashing apparatus was used, consisting of a platinum tube open at each end and fastened within a wider cylinder which is heated to a cherry-red by an electric current. The cylinder is supported by a stand in an inclined position to afford a good draft and the assay is placed in a platinum boat closely fitting the inner cylinder for good conduction of heat. The oxidation is rapid and can be promoted by a current of oxygen. In addition to this however, it is best to use an oxygen carrier. A suitable material was found in cobalt oxide as first proposed by O. Brunck in coal analysis. His method of preparation was used, ignition of cobalt nitrate, the product being superior to the commercial oxide. The final details for the leather ignition are as follows: 5 gms. finely cut leather are moistened in the platinum boat with 5 cc. 10% soda solution (omitted in

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estimating combined sulphuric acid) and then mixed with 1.5-1.8 gms. cobalt oxide. After drying 2 hours in an oven the boat is placed in the ignition apparatus and the current turned on, combustion being complete in 15-20 minutes. The contents of the boat are extracted in a beaker with hot water, filtered, the solution oxidized with a little bromine water for security, acidified with HCl and the sulphuric acid determined as $BaSO_4$ in the usual way. The following check analyses were made upon Vache leathers prepared by old pit tannage with exclusion of sulphuric acid.

| | Grams $BaSO_4$ found 1 | 2 | mean | Total $SO_3$ | Free $SO_3$ grams | per cent. found | calc. |
|---|---|---|---|---|---|---|---|
| 5 gm. leather..... | .0368 | .0376 | .0372 | .0128 | | | |
| Same+1.5 cc. N/10$H_2SO_4$ | .0534 | .0547 | .0541 | .0186 | .0058 | .116 | .120 |
| " " 2.0 " " | .0581 | .0602 | .0592 | .0203 | .0075 | .151 | .160 |
| " " 3.0 " " | .0740 | .... | .0740 | .0254 | .0126 | .252 | .240 |
| " " 4.0 " " | .0814 | .... | .0814 | .0279 | .0151 | .303 | .320 |

Cobalt nitrate solution was also used, but the swelling of the leather during combustion proved objectionable. A combustion tube with furnace may be substituted for the electric apparatus, requiring also 15-20 minutes in oxygen. The electric apparatus is preferable although expensive (190 marks, including a resistance coil which can be dispensed with); the cost of operation and materials consumed is small.

**Is a Chemical Theory Necessary to Explain the Tanning Process?** E. STIASNY. *Chemiker-Zeitung*, No. 50 through *Collegium*, 1908, Nos. 321-2, pp. 289-95.—This is in the same line as recent papers by the author on this subject and many references are made to experiments by others which are regarded as disproving the chemical theory. Some assume a hydrolysis of the hide into chemically active ingredients, but a green hide that has not gone through the usual preliminary treatment may be tanned. Moreover it has been shown that many substances which are hydrolytic decomposition products of hide such as alanine, glycocoll, leucine, etc., amido-acids and polypeptides do not act upon tannin. Glutine is the sole substance of this class which is precipitated by tannin and may be held to support the salt formation theory. The lack of stoichiometrical ratios is again dwelt upon.

That ignited alumina absorbs more tans than freshly precipitated hydroxide as shown by Wislicenus speaks for physical absorption depending upon surface action as with animal charcoal; in salt formation, the freshly precipitated base would be expected to be more reactive.

**A Peculiar Occurrence in Tan Liquors from Pine Bark.** W. EITNER. *Der Gerber*, 1908, [34], Nos. 813-5, pp. 191-2, 205-6, 219-21.—The abnormal results here discussed, observed by the writer at various times, were first called to his attention over 30 years ago. At that time a tannery in Karnthen complained that as a regular occurrence for 3 winters, from the middle of December until February, an excessive swelling of the leather was met with in the upper leather vats, giving a hard and brittle

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product. This ceased when the vats were charged with extract liquors prepared from fresh bark instead of layer bark in the usual fashion. The writer visited the tannery himself in 1875; the temperature was certainly very low but the leather showed a glassy section on cutting differing from one due to mere cold. Moreover, pigskins undergoing similar tannage, showed no swelling. The liquors on testing gave but 0.3% total acid. The swelling could not be accounted for but was subdued by adding 25 kg. salt to each vat, and this device was used in later years when necessary.

In the past winter, opportunity was offered to thoroughly study a similar occurrence in a tannery in southern Steiermark. The proprietor attributed the abnormal swelling of this leather in winter to the water, but examination showed the water to be very soft, 3 to 4° hardness and especially suited for extraction of pine bark. This was also confirmed by the bacteriological examination, 1 cc. giving 8500 spores, comprising 700 capable of acting on hide (gelatine liquefying) which is not unfavorable, especially for upper leather. A sample of the moist leather had a promising appearance but on drying became brittle, although merely in the first stage of tanning. The swelling had therefore been abnormal in character, taking place in the vats of the preliminary tannage charged with liquor extracted from fresh pine bark. A sample of the liquor (for Vache leather) analyzed 0.54% tans, 0.78% total acids comprising 0.385 acetic and 0.395 lactic acids. This exceeded (by 0.2%) the maximum of acid attributed to fermentation in pine liquors and pointed to a difference in the fermentation incites. A bacteriological examination showed instead of the usual incites of lactic acid fermentation in pine liquors (a variety of *Bacterium lactic acid Leichmann*), the presence of a nearly pure culture of *Bacterium aërogenes*. This indicated optical activity and in fact, laevo-lactic acid was found. Optically active lactic acid had not been hitherto observed in tan liquors and was next searched for from other sources. Sour pine liquors were obtained from various tanneries, including those obtained direct from sour bark, those from layaways and also from ordinary handler vats. The lactic acids here found proved to be all inactive or else in racemic combination and it was concluded that an unusual formation of lactic acid took place in the cases referred to and caused the abnormal swelling. An experiment was made which made this seem probable. It is difficult to obtain laevo-lactic acid, therefore the same liquor was employed for a laevo-lactic acid swelling and parallel with this a second was carried on with a mixture of commercial lactic acid and acetic acid of the same composition as above. In both experiments, the strengthening was gradually effected with a cold extract of fresh pine bark which had been sterilized; in the second experiment the mixture of artificial acids was added little by little. In the first experiment, fermentation took place with further formation of laevo-lactic acid and marked swelling of the leather; the liquor reached a content of 0.6% acid which then remained constant. Both leather samples were tanned to the finish; the sample from the

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laevo-lactic acid was thicker, harder and more brittle showing a dark glassy grain.

In January of this year a request for advice came from a tannery in Bohemia. A series of 12 suspender vats were employed for swelling long tannage pine leather. The complaint was concerning the formation of a thick, rough grain of dark color, easily broken. From the detailed description, this was considered a similar case to those above described and offering an opportunity for thorough study since a systematic vat tannage was employed. Accordingly samples of the liquors from the entire vat series were procured together with specimens of the corresponding hides. Examinations showed laevo-lactic acid in all the liquors. The complete analysis gave:

| Vat No. | Barkom. degrees | 100 cc. contain grams. tans | non-tans | acid (as acetic) |
|---|---|---|---|---|
| I | 9.5 | 0.3083 | 1.7687 | 0.3112 |
| II | 10.0 | 0.3195 | 1.8500 | 0.4238 |
| III | 10.0 | 0.3650 | 1.8625 | 0.4573 |
| IV | 10.0 | 0.4770 | 1.9055 | 0.4644 |
| V | 11.0 | 0.5678 | 1.8937 | 0.4860 |
| VI | 11.0 | 0.6570 | 1.9075 | 0.4836 |
| VII | 12.0 | 0.6795 | 1.9080 | 0.4836 |
| VIII | 12.0 | 0.7392 | 1.9218 | 0.4860 |
| IX | 12.0 | 0.8850 | 1.8750 | 0.5028 |
| X | 13.0 | 1.0657 | 1.8693 | 0.5004 |
| XI | 13.5 | 1.1793 | 1.8312 | 0.5028 |
| XII | 13.5 | 1.3394 | 1.7056 | 0.5004 |

This is an instructive exhibit of a very regular, normal vat tannage. In passing, the relation between gravity and tan-content may be noted. If the tan contents of vat XII be computed from its gravity on the basis of the ratio in vat I, it should contain only 0.43% tans instead of 1.34%. The discrepancy is due to the relatively greater content of non-tans and absolutely more mineral ingredients in the older liquors, affecting the gravity. The barkometer cannot properly indicate the tanning power of liquors for the initial tannage.

Returning to the main theme, the figures show that the fermentation has only proceeded to a certain limit as shown by acid contents. Very little lime was found, showing that the faults in grain were not due to this. Notwithstanding the normal composition of the liquors and the favorable appearance of most of the leather samples, these last on drying, showed that the process had been irregular. The numbers I-VI, which had been bright while soft appeared dark and horny. This was because the grain had been little acted upon (although it should have begun to form in the second vat) while the interior was lightly struck through. Not until the 8th vat could a distinct grain be perceived of a peculiar granular structure; by the 12th vat it had become very brittle. The interior of the leather however was uniformly tanned through.

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For further study of this series of liquors, they were treated with pieces of butt in the station tannery; the separate vats were strengthened with sterilized sweet pine liquor. The results were similar to the foregoing, producing a better initial tannage of the grain which finally however became also thick, rough and brittle. There was a better absorption of tan, due probably to higher temperature. Laevo-lactic acid was still present. Further evidence for the view that the active acid had a peculiar action upon hide was obtained by allowing laevo-lactic acid from sour beets to act direct upon hide. The result was similar to that observed by the writer in glacé tanning; there the butts, because of an abnormal lactic acid formation in the bran bate swell up and become gelatinous; and after tanning the leather is hard and brittle. Whether laevo-lactic acid takes part in the action of bran bate the writer does not know, but the appearances here were the same. The swelling obtained by the active acid from beets was combined with tannages of fresh pine liquor alone, and with fresh liquor from pine bark and quebracho wood. This last was used to see if by allowing the proportion of tans to acid to increase, a difference in action might ensue. In fact, the result was more favorable, there being a better tanning of the grain from the beginning and the gelatinous swelling of the hide was hindered. This agrees with experience that butts must not be intensely swelled before the grain begins to tan, if one wishes to avoid a brittle grain. Therefore as a rule, hides which are to be rapidly swelled must first be colored on the grain in sweet liquor as in American acid leather and North German sole-leather.

As a remedy for the faulty swelling of hides in pine liquors in the above cited and several other cases, the writer prescribed an addition of quebracho up to 30% to pine bark used in preparing sweet liquors. The reports returned showed satisfactory results. It seems fairly certain that laevo-lactic acid is the cause of the troubles referred to and is itself due to a fermentation flourishing at low temperatures. Our knowledge of active lactic acid fermentation is still meagre.

As to the comparison of the behavior of hides swelled in extract liquors with those of ordinary swelling during tannage in handler vats, a recent example is quoted which shows the contrast. A tanner found difficulty with his long tannage pine leather; although sufficient tan was present hides from the 5th layers were but slightly tanned. Samples were procured of the entire tannage together with the liquors, comprising those from 8 vats, 1 suspender and 6 lay-aways. The samples from the vats showed an apparently normal swelling, increasing little beyond the 3d vat, but there was little evidence of tanning before the 8th vat, whereas, a grain should have commenced to form in the 2d or 3d vat. An imperfect grain was found after the suspension which was only tanned through in the 2d lay-away. the tanning proceeded little further in the remaining lay-aways, the leather being a good half raw. Two vat liquors were examined:

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| | Vat I. | Vat VIII. |
|---|---|---|
| Tans | 0.1464 | 0.2826 |
| Non-tans | 1.8636 | 1.3324 |
| Total acids : | 1.336 | 1.260 |
| Incl. lactic | 0.660 | 0.909 |
| Ash | 0.374 | 0.243 |

The liquors are therefore much weaker in tans than those described in the earlier cases, but on the contrary much stronger in acid. The lactic acid was inactive, therefore normal. The slight action of the weak tan-liquors is explained by the excessive swelling which retards tanning. Why these liquors were so excessively acid cannot be known by the outsider, but a remedy can be found. In operating according to the old system where the fore-tanning and swelling are accomplished in handler vats, it is only necessary on the one hand to make the sour liquor weaker by drawing off more liquor from the sour bark and on the other hand to increase the tans by adding to the bark for the 2d vat, 2½% quebracho and 2½% mallet bark (coarse); to the 3d and 4th vats 5% of each material and to each of the following vats the last material, increasing 1% with each vat. In this way the pre-tanning may be so advanced that the through-tanning in the lay-aways may be regular without requiring 6 vats, of which 2 were without action in the extreme case here described.

**The Leaching of Tanning Materials and Its Supervision.** H. FRANKE. *Gerber Zeitung*, 1908 [51], No. 148.—It is generally assumed that the amount of tan left in the spent bark serves to control an extraction. This is true only to a certain extent, for if the extraction is made at too high a temperature, the tan-stuffs, although removed from the bark are in part decomposed. J. Löwe found that at 100°, 1 atmosphere pressure, 11% tans, were obtained from oak bark, and at 121°, 2 atm., only 8%, although the bark was more completely exhausted. The temperature of extraction is therefore of great importance; if too low, the extraction is incomplete, if too high the tans are partly dissociated. The proper control is reached by analysis of the liquor as well as the spent bark. The entire extract should be first collected in a measuring vessel, in which it can also settle, its tan content determined and the yield compared with the amount contained in the original bark.

**De-hairing in the Drum.** *Gerber Zeitung*, 1908 [51], No. 151.—This process is available only when the previous treatment has made the hair very loose; it has the advantage of at the same time cleaning the hides and freeing from lime. In operating, a little water is added to the hides in the drum which is run 8–10 minutes, then more water added and the drum run 5 minutes more. Finally the outlet is left open and the drum run for 10 minutes with continual addition of fresh water until the runnings are clear.

**Chamois Leather Tanning and Formaldehyde Tanning.** K. TOYOMARU from the Japanese; *Der Gerber*, 1908 [34], No. 812, pp. 177-8.—Chamois leather tannage is a combination of chemical and physical processes. A

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portion of the oil penetrates the hide-substance and becomes oxidized to a resin which coats and protects the fibres; another portion lubricates them making them soft. Still another part is decomposed, the glycerine dehydrated, forming acrolein which combines with the hide making the leather water-proof, incapable of gelatine formation.

In Europe the flesh splits of sheep skins after liming are employed. For dehairing, a bran bate is used, followed by water, draining and milling to remove more water and loosen the fibre, paying heed to the temperature. In the French process the splits are sprinkled with oil while spread on a table and then milled. By the English method the oil is gradually added during wheeling which is stopped when a strong odor is noticed. To avoid injury to the skins by overheating from oxidation, they are taken out from time to time and hung up separately in a room which is heated to promote the oxidation. It is important at the commencement of the wheeling to see that the oil has penetrated uniformly leaving no dry spots which later take up oil with difficulty. The hides are taken out of the wheel from time to time and sprinkled with oil upon the table. After the sharp odor appears, the skins are placed in a bin and the oxidation allowed to complete itself. They are next treated with lukewarm water, the excess of oil (degras) pressed out and then washed with alkali which gives sod-oil as a by-product. Afterwards the hides are spread to dry in a sunny spot, and sprinkled occasionally with water or soda wash lye to favor the bleaching, which is a slow process. A chemical bleaching is now employed with potass. permanganate, followed by $SO_2$ or oxalic acid. Marine oils are generally used in chamoisage, either liver or whale oil.

In Japan, the *himesji* leather is made very similarly. Cotton-seed oil is used and dehairing is effected without lime, the hides being laid on the bed of a brook. After cleaning the hides are treated with salt in a vat, then removed and dried, returned to the vat, wetted and oiled; they are alternately trodden in the vat and dried in the air and finally washed in the stream and bleached in the air. This process is largely physical, the leather is very firm. This is due to no lime being used, giving less loss of hide-substance; the salting also preserves hide. The cotton-seed oxidation is milder, generating less heat than in the European process. The leather is faulty in being slowly bleached and contains so much oil that it is difficult to dye.

The formaldehyde tanning process, patented by Pullmann proceeds thus; after dehairing and deliming with bran bate, the butts are brought into the formaline solution containing a little soda. Then washings with ammon. sulphate and water follow greasing with a mixture of oil and liquor, drying and currying. The writer describes some preliminary experiments made on the small scale getting the best results with 3 to 10 cc. formalin (40 per cent.) to the litre to 100 gms. of butt. Also it was found that by treatment of the butts in the drum with degras, water and gradual addition of formaline, a good leather could be obtained in a short time.

**Preservation of Hides Prepared for Tanning.** *Gerber-Zeitung*, 1908 [51], No. 153.—These may be treated for preservation by milling for 40 minutes in a solution of aluminum sulphate and salt; for 100 kg. butts, 3 kg. sul-

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phate, 6 kg. salt and 36 litres water are used. Preservation by drying is more laborious; however hides which have been dried after fleshing, especially in chrome tanning are said to yield a firmer leather especially when the single bath is used.

**Formic Acid in Tanning.** *Gerber-Zeitung*, 1908 [51], No. 153.—This is a good substitute for lactic acid and according to Lamb, it is better suited for plumping than any other acid, and is even of service in softening, acting as an antiseptic and preventing putrefaction. For this purpose, a solution of 1 liter acid in 1000 liters water is used. In tanning, formic acid has a good effect on the color of the leather and is better suited than sulphuric acid in dyeing, not injuring the grain. Because of its volatility, no trace of acid remains in the leather on drying.

**Vanadine Black.** *Gerber-Zeitung*, 1908 [51], No. 174.—This is the simplest black that could be wished, the leather needing no previous treatment as it contains itself tannin which by mere contact with vanadine solution (ammon. vanadate) forms a deep, pure black precipitate. The sole drawback is the expense 54 to 55 marks per kilo. For use 10 gms ammon. vanadate are dissolved in 1 litre of water and the solution applied to the beaten leather while still moist. If desired, the leather may be rubbed in advance with logwood decoction, the black being produced more rapidly. The logwood can also be mixed with the vanadine in advance, producing a ready black which is less cleanly and comes off to some extent.

**Discussion Relating to Large Lime and Tanning Vats.** *Gerber-Zeitung*, 1908 [51], Nos. 199, 202, 205, 208.—The subject is opened by a tanner about to rebuild. Wooden vats cannot be made very long and tight, and even so are expensive. On the contrary, cement vats are cheaper when lengthy, dispensing with a series of partitions. Notwithstanding, the operation of these long vats is less economical because the hides have to be forwarded through greater distances, increasing the labor. Handling of the hides would seem difficult in such long vats. Writer thinks, therefore, he will make new style cement pits in old style sizes.

No. 202.—This contributor is of the opinion that large lime vats are best when provided with an agitator. It is different with tan vats; these are best built of stone or cement, the location being such that the ground water is 3 meters below the surface of the tan yard, else they must be elevated. The vats should be deep enough that a large hide may be readily hung suspended at tail and hind hoofs. Two hides are thus tied together and hung over poles resting on the edges of the vats; these for large hides should be 3.2 meters deep, and need not be longer, being nearly square when 50 hides are worked hung on 25 poles. For 50 hides daily, 10 vats are needed; for 100 hides, two rows of vats, 10 each, side by side, and likewise for 150 hides, the vats being longer. The partitions are best 10 inches thick, and the vats may be narrowed 1½ feet at the bottom to save liquor, the hides being narrower at the fore-feet. It is well when the foundation is poor or exposed to shaking, to build each vat separately, that it may settle independently.

No. 205.—The question should not be whether liming should be carried out in small or large vats, but first of all how to get the maximum effect; for in-

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stance, hides for sole-leather should be treated differently from those for upper leather. They should be limed but little and the lime should act only upon the hair side, loosening the hair, similar to the sweating process. This is only possible in vats suited to the size of the hides, for heavy skins, 3¼ to 4 meters by 2 to 3 meters. The hides are then well spread out and only the hair side is reached by the lime liquors. In small vats it is necessary to crowd the hides, producing irregular folds, preventing liming. Hides in a lime should never be "handled," but only transferred to the next lime so that they lie on the reverse side. This is done singly and lifting hides in a lot from the lime by a crane is to be condemned; the strain opens the fiber and lets the lime penetrate, acting more like a bate. The shifting should be done vertically, direct from one vat to the other, a series of four limes being sufficient, shifting twice a day, sulphide should be used sparingly, if at all. Mechanical agitators (formerly Diehl's patent) have a similar effect, but the flesh is apt to suffer.

No. 208.—Paul Frank praises the foregoing article and adds that its precepts apply particularly to chrome tanning in which the greatest mistakes are made. The fundamental rule in preparation of the butts is to save hide substance, avoid dissolving it. This is obtained by rapid softening, little watering, quick liming and dehairing, avoiding all swelling, cutting, down water work consistent with good softening. Although it is possible to dehair salted hides in suitable limes without soaking, it is better to do this, without milling, however, as they then become loose and lose albumen, etc. They are better thrown into a wheel which turns once or twice a minute and treated with water containing 1 kg. caustic soda or sulphide to 1 cubic meter (=300 to 600 kg. green weight). Twenty-four hours softening should suffice. The dehairing is best done in limes "sharpened" with sodium sulphide, which can be strengthened further with soda or caustic alkali, 48 hours being enough. Protracted liming and marked swelling are just as undesirable for chrome leather as oversoaking and washing. Even with heavy hides two days soaking and three days liming are the limits.

## PATENTS.

**Automatic Clip for Stretching Leather. French Patent No. 388,866.** J. DEFOUR.

**Tanning Extract from Peat. U. S. Patent No. 899,800.** E. E. M. PAYNE, Aylesbury, England. Comminuted peat is leached with a solution of caustic alkali. The liquid extractive matter is then treated with sulphuric acid and the leather producing precipitate resulting is separated and dissolved in sodium acetate.

**Apparatus for Degreasing and Scraping Gut. French Patent No. 389,546.** E. BIANCHI.

**Process for Making Leather-Like Products from Gut. French Patent No. 389,719.** A. THIEM & CO.

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**Process of Treating Extracts of Quebracho. U. S. Patent No. 900,038.** L. POLLAK, Wilsdorf, Austria. An alleged process of clarifying extracts of quebracho wood and for rendering the tanning principles soluble in cold water which consists in adding a small quantity of alkali and water to the mud which is obtained after cooling of the liquid obtained by hot extraction after such mud has been separated from the liquid which stands above the same, and applying heat to such solution, adding a sufficient quantity of the solution thus obtained to the liquid previously drawn off from the mud to form flakes from which the liquid extract is drawn off in a clear condition after the deposit of the flakes, and rendering the phlobaphenes contained in the remaining parts of the mud soluble in cold water by mixing with the solution obtained from the mud a quantity of alkali, and heating the latter mixture with tanning extracts or liquids of higher acidity.

**Tanning with Quinones. French Patent No. 385,057.** (addition) A. SEYEWETZ AND L. MEUNIER.

**Hide Working Machine. U. S. Patent No. 900,334.** R. F. WHITNEY, Winchester, Mass.

**Machine for Cutting Leather. U. S. Patent No. 901,126.** A. W. SCHAEFER, New York.

**Production of Artificial Grain on Splits. French Patent No. 385,900.** (addition) S. PIANKO AND M. KNASTER.

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## The American Leather Chemists Association

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## CORRECTION.

Through a typographical error on line 5, page 350 of the November JOURNAL the word "satisfactory" was used instead of "unsatisfactory." With this correction the sentence will be: "It works better with some liquors than with others, hemlock being probably the most *unsatisfactory*." This refers to the use of the lime method for determining the acidity of tanning liquors, and we regret that Mr. Alsop's statement should have been so perverted.

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## PROCEEDINGS OF THE BOSTON CONVENTION.

The sessions of the convention were held at the Hotel Brunswick, Boston, Mass., on November 12th, 13th and 14th, 1908. The President, Mr. F. H. Small, presided, and Mr. W. K. Alsop, Secretary of the Association, attended to the duties of that office.

The Convention was called to order on Thursday morning, Nov. 12th, and after an address by the President, the Treasurer's report was presented and accepted.

Dr. W. H. Walker then gave a summary of the work done by the Committee on Methods of Analysis of Materials Used in the Manufacture of Chrome Leather.

Mr. F. H. Small then read the report of the Committee on the Determination of Ingredients in Mixtures of Tanning Materials, and followed this by the report of the Committee on Filtration of Tannin Analysis Solutions.

The meeting then adjourned until Thursday afternoon.

### Second Session, Thursday Afternoon.

An address of welcome was delivered by Professor Talbot of the Massachusetts Institute of Technology.

Dr. S. P. Sharples then spoke on Reminiscences of the Early Days of Chrome Tanning.

Dr. Gill, of the Massachusetts Institute of Technology, then read a paper on The Analysis of Oils.

A paper relating to American Sole Leather was then presented by Mr. C. A. Brown, of the Regal Shoe Co.

### Third Session, Thursday Evening.

Professor Graves, Director of the School of Forestry at Yale University, made an address on Forestry.

### Fourth Session, Friday Morning.

Mr. G. A. Kerr presented the report of the Committee to Investigate the Determination of the Color Value of Tanning Materials.

Mr. H. C. Reed's paper on the Color Valuation of Tanning Materials was read by Mr. Small.

Mr. W. K. Alsop then read the report of the Committee on the Acidity of Tan Liquors.

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Dr. W. H. Walker spoke on Formic Acid and Its Use in Leather Manufacture.

Mr. A. W. Hoppenstedt's paper on the Analysis of Leather was then presented by Mr. Alsop.

FIFTH SESSION, FRIDAY AFTERNOON.

Dr. Spier, of the Massachusetts Institute of Technology, read a paper on Colloids.

Mr. Small presented Mr. Reed's report as chairman of the Committee on the Chroming and Acidity of Hide Powder.

On Friday evening a Bohemian Supper was enjoyed by a full representation of those attending the Convention.

SIXTH SESSION, SATURDAY MORNING.

Mr. Wilson presented Mr. F. W. Alden's report as chairman of the Committee on Analysis and Testing of Oils and Fats.

Mr. Small then read Mr. Eachus' report as chairman of the Committee on Extraction of Tanning Materials, and followed this with Mr. J. W. Phelan's report of the Committee on Methods for Testing Commercial Acids Used in the Tannery.

The Secretary then announced that the proposed change in the by-laws, making the term of office of the President, Vice President and Secretary-Treasurer two years had been carried, as the result of the mail ballot.

The amendment to Section 15, to be known as 15-A, authorizing the Council to appoint an editor to have charge of the publications of the Association, was also carried.

The election of officers resulted as follows:

President: H. T. Wilson, Dubois, Pa.
Vice President: J. H. Russell, San Francisco, Cal.
Secretary-Treasurer: H. C. Reed, Stamford, Conn.
Members of Council: G. A. Kerr, Lynchburg, Va.; F. H. Small, Worcester, Mass.

The Convention then adjourned *sine die*.

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## PRESIDENT'S ADDRESS.

(BOSTON 1908 CONVENTION.)

*By F. H. Small.*

Our Association is passing through a critical period of its

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existence. The enthusiasm and fighting spirit which brought it into being have largely subsided into the quiet doing of the day's work as it presents itself to be done. The purpose which was mainly responsible for the formation of an Association of leather chemists, namely:—the development of a method of tannin analysis sufficiently accurate to answer for ordinary trade purposes—has been accomplished. The organization of the Association is sufficiently perfected and its support sufficiently strong so that it can go along fairly comfortably by its own inertia. There is great danger that it may be content so to drift and not make the most of its future.

Our Association, so far as your president's knowledge goes, is unique in having an active membership made up almost wholly of chemists whose time is in hourly demand for the performance of the routine duties of the work's laboratory. The investigation of methods, the study of theoretical questions, the editorial work, is done by these same chemists in moments snatched from their regular tasks or added to an already full day. After listening to a none too kindly remark by one of the members of the recent Brussells Conference relative to the comparative fewness of the original papers published by the members of our Association I could but wonder how much better off the International Association would be were it deprived of the support of the Schools. Of the twelve technical papers presented at the Conference just closed, two were from persons not directly connected with one of the schools, and of the original articles in the *Collegium* not one in twenty comes from a work's laboratory. This is not mentioned in any spirit of resentment, but merely by way of emphasizing a difficulty with which our Association must contend. For none of our members may the day's duty consist of research work in the interests of pure science. It follows directly that our Association in asking us to undertake the study of problems connected with methods or of questions whose value is largely theoretical is making in most cases a peculiarly heavy demand upon us. Only a strong feeling of loyalty to the Association and a devotion of the sort which is productive of works will suffice to meet this demand. It is therefore imperative, if our Association is to thrive, that each

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and every one of us keep our interest up to the working pitch, that we take off our coats and dig.

I would specially emphasize the necessity of each individual one of us being active. Our numbers have steadily increased both active and associate till our total membership has now passed the two hundred mark, yet if we look over the list of those who have been active in the committee work of the past year and compare this list with a similar one containing the names of those who were doing the work ten years ago, we shall be surprised at the slight difference in the names recorded. Quite too much of the strain falls on the same men who have had to bear it from the start; too few laboratories share in the burden of the work. But the indifference of a considerable number of our members works a more than merely negative injury; it actually blocks in no small measure the progress of the Association. In our By-Laws, as revised last year, is a provision that "No change in any method shall become operative unless approved by a two-thirds vote of *all* the active members of the Association." It was felt by the Committee who revised the By-Laws that in a matter so vital as a change of method, *all* the active members of the Association should have an opportunity both to test the method and to express their approval or disapproval of the same. They assumed that the interest among the members was sufficiently keen so that they would accept such an opportunity and use it gladly. In accordance with the above provision, notice of several proposed changes was sent the members during the year for their vote, but of our total active membership of 86, the largest number to display sufficient interest to vote on any one of the proposed changes was 41. While this difficulty is of course remediable by a change of By-Laws,—and such a change may be necessary,—the Association has a right to expect heartier support from its membership and I would urge upon you all a revival of that same keeness of interest which characterized the early days of our Association.

But it is not alone to our active membership that we must look for support. Our Association is poor in active members who are independent, who may work on what investigations they will and may publish the results of their investigations. The

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most of us are employed by some firm competing in the world's markets, and it is for our employers to say what we may do, what we may publish. To the enlightened generosity of many of these employers in this matter as well as to the financial backing they have given us by their associate membership is due in large measure the present successful condition of our Association. In equally large measure does it rest with them whether the Association is to be developed beyond its present estate. The proposition is certainly to some degree reversible. It is to our Association that the manufacturers must look, at least in this country, for the development of methods and theories which may assist them in their processes of manufacture.

The employer who thinks a chemist of use only to analyze raw materials and who refuses to allow the chemist to stir out of the laboratory into the works, needs educating and cannot at present be looked to for very active support of our Association. No more can the employer who believes that it is a high crime to divulge any information obtained in his laboratory be expected to assist. The In-union-there-is-strength idea seems oftentimes to fail of appreciation when topics connected with the manufacture of leather are broached, and each man of fifty is apt to believe that his one idea is worth more than the ideas of the other forty-nine combined. Of course the element of fair play comes into question and this cannot be under-estimated in considering a question such as the present. Secretiveness undoubtedly plays too large a part in the discussion of leather matters, and many a tanner for instance is years behind the procession because of clinging to some pet secret process which is really common knowledge and out-of-date.

But there is no need of venturing on dangerous ground. There is ample work on subjects of so general interest that no one could raise any objection to them as meddling with matters of a private nature. We have as yet failed to realize the fullness of meaning of the paper presented by Mr. Alsop at the last annual meeting of our Association. A rapid method for the determination of soluble hide in limes and liquors is much needed, though possibly Prof. Stiasny in his paper presented at the recent Brussells Conference has partially solved the prob-

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lem. The relationship between the composition of a liquor and its plumping qualities, a subject opened recently by Claflin and Griffith, needs much further study. Our brethren of the International Association would doubtless welcome gladly any help we might offer toward the solution of the broad question of the cure and disinfection of skins and hides, a subject presented for their consideration at the Brussells Conference by Mr. Seymour-Jones and of immediate and practical interest to our tanners, in view of the recent action of our Government. It is needless to multiply instances. The essential point to be kept constantly in mind is that on the friendly and active support of the manufacturers must the future of our Association largely depend, not on their financial support, though that is necessary, but on that broad-mindedness which encourages the chemists to devote a portion of the time belonging to the manufacturer to the study of problems not necessarily immediately convertible into dollars and cents. Our country is almost alone among the great nations of the world in having no schools for the teaching and investigation of matters connected with the leather industry. The Leather and Paper Laboratory at Washington is doing something and we have an occasional paper from some one of the Technical Schools, but neither the government nor the tradespeople have seen fit to give us anything to compare with the schools abroad.

A criticism has been made of our Association to the effect that we have neglected the upper leather, the chrome leather, the patent leather manufacturer, as well as the shoe maker, but I submit that it is rather they that have neglected us. We have made various overtures to them, in particular have striven hard to interest the chrome people, but have met with so little encouragement that we have been compelled temporarily to abandon the attack.

There is a question of policy which it may be well to consider briefly here. We have been accustomed to appoint our investigation commmittees and ask them to report at a definite time, bringing pressure to bear if results are not forthcoming at the appointed time. Possibly this best suits our condition, but it has seemed to me that very likely we were losing by this procedure. A too frequent change of officers is much like sending

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a runner back to the starting line for a fresh start at the end of every mile in a ten mile race, so that while he runs two miles in his second trial he has had the first mile to run all over again, and so on. For this reason I hope that the proposed change in the By-Laws lengthening the term of office of our president, vice president and secretary-treasurer, may meet with your approval. As regards the committees, I believe it would be more profitable to continue them in office so long as they are able to produce results, expecting them to give the subject German treatment, as we are wont to express it. Possibly occasional changes of personelle might be found desirable or necessary in part, but let the committee keep digging until it gets somewhere.

The result of steady conscientious digging at a thing is shown by the wonderful progress made by our JOURNAL under the able editorship of Mr. Teas, whom the Association has been fortunate in retaining as editor of the Journal since its inception. Were it necessary to give an excuse for our existence we could point to our JOURNAL as alone sufficient. Largely through its instrumentality our Association has become known and recognized till it enjoys today a prestige truly remarkable when we consider the youthfulness of the Association.

We have all the ingredients of success. Let us see that we use them to achieve a great success. Believe in the Association; use every effort to interest our associate members actively and practically in the work and aims of our Association; and finally work for the Association each one of you with a realization that on your efforts depends not merely the success of our Association but in no small measure the advancement of the industry whose prosperity we all have so much at heart.

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## THE COLOR VALUATION OF TANNING MATERIALS.[1]

*By H. C. Reed*

The determination of the color value of vegetable tanning materials have ever been a fruitful subject for controversy among chemists connected with the leather trade and its allied industry,

[1] Read at the 1908 Boston Convention.

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the tanning extract trade. The question is assuredly an all-important one, and for this reason the omission of a standard method for color valuation from our official methods is significant of the unreliability of the suggestions that have been made as solutions of the vexatious problem.

Two methods for color testing have occupied our attention more particularly; the one based on the color obtained by the actual tannage of pelt, and the other based on the separation of the color of a solution of the material into its ultimate components of red, yellow and black as given by the tintometer measurement.

The former method, and the one almost exclusively used in this country, is open to one very serious and apparently insurmountable objection, which is the impossibility of obtaining pelt that will give sufficiently uniform and consistent results. Not only will the skins of sheep, calf or cow give varying color valuations on the same tanning material, but portions taken from different parts of the one skin will, though in less degree, produce irreconcilible results, and this despite the amount of care exercised in the previous preparation of the pelt. That a method for color valuation must have as a fundamental principle the assurance of being capable of yielding at least an approximation to uniformity seems an assertion unlikely of contradiction. The criticism is also rather widely prevalent that color tests made by the tanning of pelt on a laboratory scale is not representative of the results obtained in practice, on a commercial scale. This is unquestionably true, but the criticism would seem to lose much of its force in view of the fact that no two tanneries will produce leather of identical color with the same tanning material. Too great stress has in the past been laid upon this phase of the situation. It is manifestly absurd for us to attempt to duplicate in the laboratory the many and varying conditions of tannery practice and environment. To the mind of the writer, the question would seem to find its solution in the answer that we have been forced to give to so many of the problems that have confronted us in the past, "An empirical method." We have admitted for some time the truth of this answer pertaining to our method of tannin analysis, and more recently its application to the extraction of crude materials in the laboratory has become evident. Most certain is it true that

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if one tanner produces leather of a certain color with a certain extract and another tanner produces leather of a quite different color with the same extract, it is a hopeless task for the chemist to reconcile two such opposing results when he is unable even to duplicate his own.

The question then arises, have we a panacea for the ill in a method of tintometer measurement? Have we in this method a satisfactory answer to the demands of empiricism, uniformity and consistency? Have we here a method that appeals to the demand of the trades as a satisfactory and tangible basis for agreement? The tintometer measurement may inform us as to the relative proportions of red, yellow and black present in the solution of a tanning material, but leaves it to our imagination to interpret what will be "the outward and visible sign of an inward and spiritual grace." As to uniformity, it has yet to be proved that sufficient agreement is possible between analysts in reporting tintometer measurements where so much depends upon the capability of matching shades as in this method. Added to this it would appear very doubtful whether in the absorption of color in the tanning process the reds, yellows and blacks are fixed in the proportions of tintometer measurement. Unless it is true that all the color present in a given solution is absorbed by the pelt, an entirely erroneous impression is gained from tintometer readings. It is true however, that on this score there can no just complaint be made as to the empiricism of the method, except only in the imaginative deductions from the readings which from unequal absorption of color compels us to attempt the practically impossible feat of picturing from the same tintometer reading a different color effect. The phenomenon of selective absorption would seem to strike a death-blow to the effectiveness of the method inasmuch as it eliminates any certain basis of comparison. If the theoretical assumption that tintometer measurement will indicate the true color value of a tanning material is sound, then, since the sum of the readings is the actual color of the solution read, we must have in the color of the solution itself a visible protrayal of its color value. But that the color of a tannin solution is a true criterion of the color of the leather produced from it

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is far from being a safe presumption. Processes of clarification and decolorization are pronouncedly inimical to such a theory.

A consideration of the two methods suggested that the former would possess many advantages over the latter, and possibly all the requirements necessary for a practical method, provided the evils attendant upon uniformity of pelt could be rectified. Inasmuch as these evils seemed inherent to the pelt, material other than skin was sought. Experiments were made first with cotton cloth. Solutions of various tanning extracts were made, standing at 25° Barkometer, and the cloth, after thorough wetting, allowed to steep in the liquors for a definite period. The cloth was then squeezed from the liquor, washed thoroughly with water at ordinary temperature and permitted to dry after spreading on a glass plate while still wet. The results of the tests are presented to you accompanied with a key indicating the various tanning materials employed.

Believing that the method might be susceptible of giving better result by the substitution of wool cloth for cotton, further tests were made with this material along the same lines as with cotton cloth. Another series of tests were made with a good grade of white broadcloth, and the results of both series of tests submitted for your inspection.

The color valuations where broadcloth is employed appear the most satisfactory. Your attention is directed to the fact that the method will discriminate between extracts produced from the same crude material, doubt of which was expressed prior to the completion of the tests.

The claims advanced for the method are that it is capable of producing uniform and consistent results, that it is tangible, not addressed to our imaginative faculties; that it is empirical, in so far as empiricism is necessary. There would seem but little likelihood of variation in the broadcloth, and if such were true all differences could be avoided by the purchase of a sufficient supply of the material and distribution of the same from a central source.

The method suggested is admittedly only in its tentative stages and details yet remain uncompleted. The hope is expressed that the proposal may meet with the fullest discussion and criticism.

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## IODINE VALUE OF OILS.

*By Dr. Louis E. Levi and E. V. Manuel, S. B.*

In the management of the laboratory as well as in the factory the principal factor to be considered is:—To obtain the greatest efficiency at the least cost. The laboratory of the trade-chemist as well as that of the manufacturer must be run on this plan in order to show the minimum percentage of cost. The American chemist is often handicapped by his European *confrere* by the prices of the chemicals which are necessary for the successful plying of his profession. Small reductions in cost of operating expenses tend to make the photograph of the ledger of the trade-chemist, at the end of the year, glow with that warmth of pleasure equaled only by an increasing clientage.

The manufacturer who has installed a laboratory, is also well pleased with the results aside from the benefits derived. The chemist so employed has smooth sailing and can more easily obtain the necessary means to carry on his investigations and broaden his field of work. With this object in view and at the same time to study the new materials offered by the chemical industry, we have made a study of new materials to take the place of some used in the analysis of oils. Chloroform has long been used in the determination of the "Iodine Value of Oils," and we have made experiments with carbon tetrachloride and pentachlorethane to take the place of this easily decomposable chloro form. The following are the results obtained, compared with the old method:—

| | Iodine values | |
|---|---|---|
| Samples No. 1 | By $CCl_4$ | By $CHCl_3$ (Hanus) |
| Cod liver oil | " 154 | " 154 |
| Olive oil | " 85.3 | " 85.1 |
| Sperm oil | " 83.5 | " 83.8 |
| Neatsfoot oil | " 75.01 | " 74.7 |
| "Tan" oil | " 32.50 | " 33 |
| Samples No. 2 | " $C_2HCl_5$ | " $CHCl_3$ (Hanus) |
| Cod liver oil | " 158 | " 157 |
| Olive oil | " 86 | " 85.1 |
| Sperm oil | " 84.4 | " 83.8 |
| Neatsfoot oil | " 72.6 | " 72 |
| "Tan" oil | " 33.1 | " 33 |

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The above tests show to us that either carbon tetrachloride or pentachlorethane can be substituted for chloroform and yield excellent and reliable figures. We have also found that the chloroform in order to give good and accurate results, must be kept in a dark cool place and freshly distilled before using, as it is liable to decomposition by the action of heat and sunlight as is well known by surgeons, who wish to employ it as an anesthetic.

We have adopted the use of $CCl_4$ in preference to $C_2HCl_5$ on account of its comparative low cost and being easily obtainable. It is easily purified and will keep without decomposition with little or no care. We employ two methods for the purification of carbontetrachloride, either of which gives good results:—

*Purification of Hyposulphite of Soda.*—Commercial carbontetrachloride is shaken with a solution of "Hypo" at intervals of one-half hour for about two hours. Let settle and separate the two layers in a funnel. The $CCl_4$ is then shaken with a 5 per cent. solution of NaOH every 15 minutes for one hour. Separated, again dried with chloride, fused and distilled.

*Purification by Iodine.*—The $CCl_4$ is shaken with Hanus' Iodine solution the same length of time, then treated with a solution of 5 per cent. NaOH, separated, dried with $CaCl_2$ and distilled.

As either of the above methods of purification yield an excellent product the chemist can use the one which best suits his fancy, without the fear of unreliable results.

We are also experimenting on the use of dichlorethylene, trichlorethylene, perchlorethylene, tetrachlorethane and pentachlorethane in the extraction of fats to take the place of petroleum ether or benzene.

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## THE NINTH CONFERENCE OF THE I. A. L. T. C.

*By F. H. Small.*

The Ninth Conference of the International Association of Leather Trades Chemists was held at Brussels from Sept. 21st to 23rd inclusive. The sessions were held in the Maison des Medicins, one of the old guild houses in the Grand Place, a most interesting spot. The Conference was characterized by the large

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number of members present from widely separated parts, the comparative lack of social functions and the important and valuable progress made toward a better formulation and understanding of analytical methods relating to the tanning industry.

In attendance were members from India, Australia and America, as well as from most of the European countries and England. Socially, there was a reception to the arriving members by the members of the Belgium section at the Maison des Medicins, on Sunday evening the 20th inst.; on Tuesday evening a party was made up to attend a performance of the modern French opera "Le Chemineau" at the Theater Royal de la Monnaie, and on Wednesday evening the usual dinner was held in the Taverne St. Jean. As this made up the list of social functions the attention of the members was little diverted from the prime interests of the Conference and a large amount of work was harmoniously and satisfactorily gone through.

Before giving an account of the technical matters discussed it is perhaps well to mention various items of general business transacted. Of marked interest and importance was the election of officers which resulted in the choice of Professor Henry R. Procter of Leeds as President, Professor Louis Meunier of Lyons, Treasurer; and the re-election of Doctor J. Gordon Parker of London as Secretary. Prof. Dr. Haenlein, the retiring treasurer, having declined to serve again, was given a vote of thanks for his careful and conscientious custody of the funds of the Association, which by the way were reported in a most satisfactory condition. Dr. Parker was voted a gold metal in recognition of his long and efficient services as Secretary of the Association, he having been one of the founders of the Association and having served steadily as its Secretary ever since. The Klipstein prize was awarded to Prof. Procter and the Seymour-Jones prize to Prof. Dr. Edmund Stiasny of Vienna.

On the recommendation of the Executive Committee it was voted to increase the size of the *Collegium* by giving it a cover, the first page to be used for all non-technical matter, business announcements, etc. relating to the Association and the remaining pages given over to advertisements. Dr. Parker announced that he had already been promised advertisements by

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several of the American Colleagues. In this connection a vote of thanks was given the Editor of the *Collegium,* Mr. Schorlemmer, for his efficient services as Editor.

The following resolutions were passed by the Association:—

I. The Conference tenders the members of the International Commission on Tannin Analysis and their co-workers its heartiest thanks for their unselfish labors. The Conference begs the Commission to continue its labors and to publish at intervals the results of its study of the various matters submitted to it, together with its recommendations. If the Executive Committee considers the reasons given for the recommendations satisfactory and no member of the Analysis Commission or of the Executive Committee raises any objection to the same during a period of three months from the date of publication, the Executive Committee is hereby commanded to declare the recommendation of the Commission *Official.*

II. Only those methods of analysis decided upon and authorized by the whole Association may be designated as *Official.* It is not permissible in rendering opinions or Analytical reports to refer to methods as *Official* which have been superseded.

III. Copies of opinions and analyses given out for trade purposes must be in full and with date and analysis number.

IV. The Executive Committee is authorized to appoint such Commissions as may seem to it desirable. The President of the Association shall be Ex-Officio member of all such Commissions.

The purpose of these resolutions is rather evident on the face of them, some of them being intended to stop various trade evils while the last had in mind the broadening of the scope of the active work undertaken by the Association. The desirability of this was pointed out by Mr. Seymour-Jones in a paper on "The Future Operations of the I. A. L. T. C." in which after calling attention to the fact that the present methods of Tannin analysis were on a fairly satisfactory basis, he urged the appointment of Commissions to study such matters as the curing, preserving, and disinfection of hides and skins, etc.

The above gives a brief outline of the general business passed upon by the Conference. The greater portion of the time of the Conference was devoted to the reading and discussion of papers

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on purely technical matters, and in particular to a careful consideration of the second report of the International Commission on Tannin analysis with the included recommendations.

The Commission in its first report having in mind the desirability of drawing up a set of regulations which should be sufficiently comprehensive to include the method of the American Leather Chemists Association, as well as the particular ideas of the Commission, divided its recommendations into two parts, the first under the head "General Regulations" being broad in scope and the second under the head "I. A. L. T. C. Method" being narrowed in various particulars and much more detailed. The main value of the "General Regulations" is in defining a common ground on which it is hoped to map out what may ultimately become a universal method of Tannin Analysis. The directions under the head "I. A. L. T. C. Method" outline the method which it is obligatory upon the members of the Association to follow in all public analytical work.

In its second report the Commission recommended leaving paragraph 1. the "General Regulations" relating to extraction and making up of analysis solutions, unaltered. This came in for a general discussion however, it being shown that as it stood the paragraph did not permit the use of the method of extraction employed by the A. L. C. A. It was finally voted to amend the paragraph to read:—"The solution for analysis must contain between 3.5 gms. and 4.5 gms. of tannin matter per litre and solid matters must be extracted so that the greater part of the tannin is removed at a temperature not exceeding 50°C. or if the Teas extractor be used the first portions of the extract shall be removed from the influence of heat as soon as possible." It seems doubtful whether the method of extraction now employed by the members of the A. L. C. A. has received the consideration it deserves at the hands of the members of the I. A. L. T. C. and whether carefully conducted series of tests in one of the English or Continental Laboratories might not serve to break down the present prejudice against the American method. The feeling seemed to be that not merely was there danger by the Amercan method of destroying tannin by the heat employed, but that the later extractive matters were only woody compounds and

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not tannin. So long as tannin is defined as matter precipitable by a gelatine-salt solution, however the latter criticism seems invalid, and the writer believes the first criticism unfounded and the result of a lack of sufficiently careful and extended tests of the method as defined .

A change in paragraph 2. was recommended by the Commission relative to the temperature of filtration as also the enlargement of the paragraph to include a prescription relative to drying. After a rather extended discussion it was passed as follows:— delete last sentence and substitute, "Filtration shall if possible take place between the temperatures of 15°C. and 20°C., but if from climatic or other reasons a higher limit is adopted, this shall be stated on the report. Evaporation to dryness shall take place at a temperature between 98°C. and 100°C. in shallow flat-bottomed basins, which shall afterward be dried until constant at the same temperature and cooled before weighing for not less than 20 minutes in air-tight desiccators over dry calcium chloride."

In connection with the question of filtration the writer urged the desirability of settling as soon as possible upon one definite method and expressed a hope that the Reed Asbestos-Kaolin Method might prove to have sufficient merit to warrant its universal adoption. He gave details of the method and has the promise that it will be tried out in some of the laboratories.

Paragraph 2. as passed allows a wide range of drying apparatus and as regards the prescription for drying to constant weight must not be taken too literally, for it is doubtful whether a mixture of bodies such as is found in an extraction residue can be brought to constant weight. As a compromise it is probably successful. The Continental Chemists seem rather generally to prefer as a drying apparatus the Moeslinger *Trockenschrank*, a steam oven in which each dish is placed in a separate compartment; the English Chemists on the other hand prefer the Vacuum oven. Comparatively few seemed to have tried the Combined Evaporator and Dryer, and of these few still fewer had a good word to say for it. Some of the objections raised were the length of time required for the evaporation and the drying whereby it was argued than an error due to oxidation was introduced or increased. Another objection was inability to secure concordant

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results. As these objections are contrary to our experience in America it was interesting to try to find the cause, and the writer feels sure from what he saw that in part, at least, they are the result of faulty design and construction of apparatus.

Paragraph 3. was altered to correspond with Paragraph 2. in the matter of drying. The question of the best method of determining the moisture in solid extracts received some attention, it being stated that the direct and indirect determinations did not correspond.

Paragraph 4. was so altered as to make the limiting values of Chrome permissible in the Chromed hide powder .2 and 1.0 instead of .5 and 2.0. The revised limits will permit the use of hide powders chromed by either the method of the A. L. C. A. or the I. A. L. T. C., whch the former limits did not.

The Commission recommended leaving paragraph 5 of the official I. A. L. T. C. method unaltered; but after a general discussion it was decided to alter the paragraph to read, that filtration should take place at 17.5 degrees, Centigrade, instead of allowing a temperature range of from 15 to 20 degrees, Centigrade. Paragraph 6 was left unaltered. It was voted to alter paragraph 7. to read as follows:—"Hide powder shall be of woolv texture, thoroughly delimed, preferably with hydrochloric acid and shall not require more than 5. cc. or less than 2.5 cc. of N/10 caustic soda to produce a permanent pink with phenolphthalein on 6.5 grams of the dry powder suspended in water. If the acidity does not fall within these limits it must be corrected by soaking the powder before chroming for 20 minutes in 10-12 times its weight of water, to which the requisite calculated quantity of standard alkali or acid has been added. The hide powder must not swell in chroming to such an extent as to render difficult the necessary squeezing to 70-75% of water, and must be sufficiently free from soluble organic matter to render it possible in the ordinary washing to reduce the total solubles in a blank experiment with distilled water below 5 mgs. per 100 cc. The powder when sent out from the makers shall not contain more than 12 per cent. of moisture, and shall be sent out in airtight tins." The remainder of the paragraph was left unchanged. There was some discussion of the desirability of raising the upper limit of acidity to at least 1 cc. N/10 alkali per 1 gm. dry hide powder, but the paragraph was passed as above. It is doubtful

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whether so low an acidity as the upper limit adopted by the Association will work out satisfactorily when some oak bark and hemlock extracts are analyzed. In this connection the writer presented some data obtained by this year's committee on hide powder of the A. L. C. A. tending to show that the non-tannin figures obtained with hide powder chromed by the I. A. L. T. C. and A. L. C. A. methods respectively varied much more widely in the former case with differences in the texture or the acidity of the hide powder than in the latter.

A change was adopted in paragraph 8. limiting the permissible concentration at which liquors might be analyzed to 10 gms. of total solids per litre, and a new paragraph 9. adopted as follows:— "All evaporations shall be rapidly conducted at steam temperature in shallow flat-bottomed basins of not less than 6.5 c.m. diameter, to apparent dryness, and shall be subsequently dried at 100°C. for 30 minutes in vacuo or for 90 minutes in a water or steam oven with small compartments, and subsequently cooled in small air-tight desiccators over dry calcium chloride for at least 20 minutes. Not more than two dishes shall be placed in one desiccator."

These latter changes led to comparatively little discussion. Those portions of the sessions of the Conference not accounted for above were devoted to the presentation and discussion of various technical papers. The remarks of Mr. Wood in connection with his paper on "Compounds of Gelatine and Tannin" were of particular interest as bearing on the question of tannin analysis. His final conclusion based on a thorough study of this subject was that there is no real chemical compound of hide substance and tannin, that the hide powder method must of necessity be a purely empirical method, in which the sole hope for concordance lies in a careful and complete definition of every last detail of procedure, that consequently future progress is to be expected only along the line of a closer prescription of details.

It is not practicable in this report to attempt to give any detailed account of the various papers presented. A most interesting discussion of the theory of the tannin process was participated in by Messrs. Meunier and Stiasny apropos of the papers presented by each. Another paper by Stiasny on "A Rapid Method for the Estimation of Soluble Hide in Soaks and Limes" attracted

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especially favorable notice. It may be said that the papers were for the most part all of high grade, and in short the whole Conference may be summed up as eminently successful.

## NOTE ON THE IODINE VALUE OF PARAFFINE OIL.

(SPEC. GRAV. 0.906).

*By I. Dreyfus.*

Paraffine oil requires a large excess, about 80 per cent. of the amount of Iodine solution "Hanus" added, and the time of action should be at least 8 hours for the absorption of Iodine, according to the following tests:

| | Excess of iodine solution. Per cent. | Time of action | Iodine value |
|---|---|---|---|
| 1 | 62.5 | ½ hour | 16.7 |
| 2 | 72.0 | ½ hour | 23.8 |
| 3 | 85.6 | ½ hour | 35.9 |
| 4 | 86.9 | 3 hours | 49.4 |
| 5 | 86.0 | 6 hours | 53.1 |
| 6 | 85.7 | 8 hours | 57.0 |
| 7 | 85.4 | 20 hours | 57.9 |
| *Iodine Value by Hübl Waller's Method—* | | | |
| 8 | 89.2 | 6 hours | 11.0 |

## CURRENT ARTICLES.

*The Leather Manufacturer.*

TANNING FOR WELT LEATHER. October.

SPLITTING HIDES FOR CHROME LEATHER. *L. A. Fleming*, October.

CHROME *vs.* BARK TANNED LEATHER. October.

DRUM TANNAGE. November.

PICKLED SHEEPSKINS. November.

DETRIMENTAL EFFECTS OF IRON ON LEATHER. November.

*Collegium.*

NINTH CONGRESS OF THE INTERNATIONAL UNION AT BRUSSELS. (Proceedings). Sept. 26, Oct. 24.

SECOND REPORT OF GERMAN COMMISSION ON TANNIN ANALYSIS. (Conclusion). *Dr. Paessler*, Oct. 3.

THE FUTURE OPERATIONS OF THE I. A. L. T. C. *Alfred Seymour-Jones.* October 10.

THE DETERIORATION OF LEATHER AND THE INFLUENCE OF GAS FUMES. *M. C. Lamb*, Oct. 10, 17, 24.

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*Der Gerber.*

THE MANUFACTURE OF POLISHING LEATHER. *W. Eitner*, Oct. 1.

MYRABOLAMS IN EXTRACT MANUFACTURE. *J. Waldika*, (concluded). Oct. 1.

THE ACTION OF THE FALSE BARK BEETLE ON PINE BARK. *W. Eitner*, Oct. 15.

THE FINANCIAL SIDE OF TANNIN ANALYSIS. *R. B.*, Oct. 15.

*Gerber Zeitung.*

SPLIT LEATHER WITH IMITATION GRAIN. Sept. 26.

MANUFACTURE OF PATENT LEATHER. Sept. 28.

NOTES ON LARGE VATS. Sept. 29, Oct. 3, 9, 12, 17.

THE GREASING AND AFTER TANNING OF HARDENED UPPER LEATHER IN ONE OPERATION. Oct. 6.

EMPLOYMENT OF OXALIC ACID IN TANNING. Oct. 7, 10.

TANNING AND CURRYING OF KANGAROO LEATHER. Oct. 13.

*Le Cuir.*

SULPHIDE OF SODA IN DEPILATION. Oct. 15.

RAPID TANNAGE. (Historical). *André Gagnard*, Oct. 15.

FRAUDS IN CRUDE HIDES. *A. Schmidt* (current), Oct. 15.

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## REVIEWS.

**Second Report of International Commission on Tannin Analysis, Conference 1908.** H. R. PROCTER. *Collegium*, 1908, No. 326, pp. 353-6.—A few changes and additions are recommended; the limits 0.2 to 1 per cent. for chromium contents. (7.) Six and one-half grams dry hide powder should require not more than 5 nor less than 2.5 cc. N/10 NaOH otherwise correct by soaking before chroming in water to which requisite alkali or acid has been added; it should not swell so that squeezing to 70-75 per cent. water contents is difficult. Ordinary washing should give solubles below 5 mg. per 100 cc. Kaolin to be used only when needed. (8.) Concentration should not exceed 10 gms. per litre solids. (9.) Evaporate at steam temperature in shallow basins not less than 6.5 cm. diameter, dry at 100° in vacuo 30 min., or 90 min. in steam or water oven; cool in desiccator over $CaCl_2$ 20 min.

Dr. Meunier tested the effect of increasing the strength of the chroming solutions. The analyses are for non-tans in chestnut extract.

| | Official | Double official | Triple official |
|---|---|---|---|
| With Paessler Hide Powder | 15.78 | 15.05 | 14.74 |
| " American " " | 15.07 | 14.44 | 14.21 |

The results with ready chromed hide-powder are not yet considered sufficiently concordant to permit its adoption.

**Estimation of Non-Tans.** H. R. ZEUTHEN. *Collegium*, 1908, No. 326, pp. 366-70.—Ready chromed hide powder would simplify operations for the

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analyst but the usual manipulations with wet hide according to the official method, washing, squeezing and weighing, would still include the principal sources of error. To avoid these, the writer uses the filter bell as in Veit's method (*Abstr. this JOURNAL*, 1908[3] No. 10, p. 319) for previously washing the chromed powder and proceeds with detanning precisely according to the official method. Weak chromed hide powder equivalent to 5.5 gms. dry is stuffed into the bell which closed with gauze is placed in distilled water to the neck; when the hide is thoroughly wet, the stopper is removed and the neck filled with distilled water. The stopper is replaced (without including air bubbles) and the circulation begins; after 30 cc. washing, the bell is taken apart, the moist powder placed in a tared glass and made up to 40.5 gms. total. The 100 cc. of tan solution are added and shaken in the usual way. The 35 gms. of water are taken account of in the computation.

Less hide is used than in the official method, but has shown itself to be sufficient in all cases and to give the same results. It is possible however to use 6 gms. or even 6.5 gms, of the latest Freiberg preparation. A series of comparative analyses of several extracts with two brands of Freiberg ready chromed hide powder are cited. While 30 cc. washing is set as the minimum, this may be exceeded at will. It was found that the first 10 cc. removed nearly all the solubles and after that there was a small amount extracted proportional to the amount of washing. The non-tan determination, however was not affected, the result being the same for any degree of washing. This is convenient in preparing hide-powder in advance for use.

**Tan-Stuff Analyses.** *Gerber-Zeitung.*, 1908 [51], No. 227.—The union of German extract manufacturers publish comparative analyses of a guaranteed pure quebracho extract as an example of what can be expected from the official method.

| | Filter method | | | Shake method | | |
|---|---|---|---|---|---|---|
| Laboratory | Tans | Non-tans | Insoluble | Tans | Non-tans | Insoluble |
| 1 | 36.1 | 3.8 | 1.4 | 32.1 | 4.7 | 4.0 |
| 2 | 35.4 | 3.8 | 2.0 | 35.9 | 4.1 | 0.8 |
| 3 | 36.3 | 3.4 | 1.2 | 32.2 | 8.6 | 0.5 |
| 4 | 35.5 | 3.3 | 2.2 | 34.2 | 4.2 | 2.3 |

**Second Report of the Analysis Commission of the German Section.** J PAESSLER. *Collegium*, 1908, Nos. 328-9, pp. 383-96.—The commission which was continued at the Frankfurt meeting has directed its labors towards explanation of the discordant results obtained by the official method. The comparative analyses were made by Drs. Moll, Philip, Sichling, Arnoldi and Veit. Five brands of hide powder were used.

(1) white, Freiberg, previous ..... 5.5 per cent. soluble
(2) chromed, " " ..... 2.4 " " "
(3) white " new ..... 2.1 " " "
(4) chromed, " " ..... 0.5 " " "
(5) white, American ..... 2.1 " " "

The solubles were determined by shaking 6.5 gms. (dry) with 100 cc. of water.

Five extracts were analyzed, I. Oak Wood; II. Quebracho, Solid; III.

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Chestnut Wood; IV. Quebracho, Sulphited; V. Pine Bark. The condensed results only are here quoted.

| Ext. No. | Average per cent. non-tans. for different hide powders. 1. | 2. | 3. | 4. | 5. | Greatest differences in non-tans. for different hide powders. 1. | 2. | 3. | 4. | 5. |
|---|---|---|---|---|---|---|---|---|---|---|
| I | 12.3 | 12.2 | 11.9 | 12.3 | 11.9 | 0.7 | 0.4 | 0.25 | 0.75 | 0.55 |
| II | 7.9 | 7.8 | 7.6 | 7.9 | 7.9 | 1.0 | 0.6 | 0.4 | 0.45 | 0.9 |
| III | 13.3 | 13.4 | 12.9 | 13.5 | 12.7 | 1.0 | 0.8 | 0.65 | 0.5 | 0.95 |
| IV | 9.0 | 8.7 | 8.5 | 8.8 | 8.7 | 0.4 | 0.65 | 1.05 | 0.25 | 0.55 |
| V | 24.0 | 23.8 | 23.6 | 23.9 | 24.6 | 0.75 | 1.15 | 0.55 | 0.35 | 1.1 |
| Average | 13.3 | 13.2 | 13.3 | 13.3 | 13.2 | 0.77 | 0.72 | 0.58 | 0.56 | 0.81 |

The concordance of results by the individual analyst was much better than those of the first report, showing improvement by practice. As to the different hide powders, the results are much the same. The opinions of the several members of the commission are given separately, agreeing in the main. The new Freiberg powder is more satisfactory than the old; the American granular hide-powder handles and washes better than the woolly Freiberg brand but does not filter so clear, requiring kaolin, which in some cases absorbs non-tans. Veit's method (first report) has not been further tested. Ready chromed hide powder is recommended.

**A Tan-Stuff Reaction and Its Application.** E. STIASNY. *Der Gerber*, 1908, Nos. 815-16, through *Collegium*, 1908, Nos. 332-33, pp. 419-26,—The author has previously published an article concerning the reaction of formaldehyde on tan-stuffs. (*Der Gerber*, 1905, p. 186). On boiling with formaldehyde and HCl, all catechol tan-stuffs are completely precipitated; pyrogallol tan-stuffs remain clear or give (when gallic acid or tannin are present) only partial precipitation and the filtrates give distinct reactions for tan-stuffs.

To carry out the test, 50 cc. of the tan solution are boiled 10 minutes (invert condenser) with 10 cc. formaldehyde 40% and 10 cc. HCl (1 : 1) then cooled and filtered. The filtrate is tested with 1 to 2 drops gelatine-salt solution and also with about 1 cc. ferric alum (1%) with addition of 5 gms. sodium acetate. Pyrogallol of tan-stuffs give a blue or violet ring (avoid shaking).

I. This reaction as formerly stated, may be used qualitatively but not quantitatively. The gravimetric applications since published by others are not regarded as reliable. The errors are due to precipitation of non-tans by formaldehyde as shown by author (*Gerber*, 1905, p. 216). This difference is small for quebracho which has led to the method being recommended.

II. Another application of the reaction is for the qualitative detection of pyrogallol tan-stuffs in presence of catechol tan-stuffs, as for instance myrabolams in quebracho or mimosa extract. 5% may be detected; the intensity of the blue increases with larger amounts, enabling a rough estimation of the amount of adulteration. The author has found this test reliable and employed it in over a hundred cases.

III. Contrary to the views of Jean and Frabot, the author does not consider the formaldehyde precipitation suited for the quantitative separation of protocatechu and pyrogallol tan-stuffs. Experiments are detailed showing

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that considerable amounts of pyrogallol tans are included in the precipitates as well as non-tans.

IV. A reaction of limited application depends upon the fact that the precipitation of protocatechu tans only takes place in the presence of mineral acids without however fixing these. By adding a known amount of standard HCl and titrating the filtrate, any acids present in the original liquor show themselves by increase in alkali used. Unfortunately most acid liquors are not free from pyrogallol tans.

V. The reaction may be employed to investigate the relative rates at which different tanning substances are taken up by hides from mixtures. Laboratory experiments have not been made in this direction, and opinions vary among tanners. The method here used was to treat pieces of butt with the mixture in question, and at regular intervals precipitate the formaldehydes. The weight of the precipitate was compared with that of the remaining total residue in solution. If protocatechu tans are taken up in greater amount by the hide, the ratio would decrease and *vice versa*.

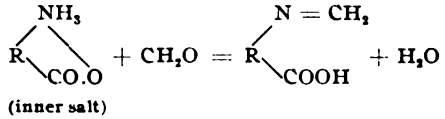
RATIO OF PRECIPITATE TO TOTAL RESIDUE IN PERCENTAGE.

| Hours | Pine and oakwood | Pine and chestnut wood | Quebracho and oakwood |
|---|---|---|---|
| 0 | 30.1 | 23.7 | 49.0 |
| 6 | 18.5 | .... | 16.2 |
| 24 | 14.8 | 17.65 | .... |
| 48 | .... | 15.85 | 10.4 |
| 72 | 8.9 | .... | 9.9 |
| 96 | .... | 14.7 | .... |
| 144 | .... | 12.1 | .... |

The figures show that in the three mixtures there was a more rapid absorption of pine, pine and quebracho respectively. The results are regarded as merely qualitative.

VI. Similar experiments showed that in an oakwood-mangrove mixture, the oakwood tans dialyzed most rapidly.

**A Rapid Method for the Determination of Dissolved Hide in Soak and Lime Liquors.** E. STIASNY. *Collegium* 1908, Nos. 326-7, pp. 371-5.—Of the methods previously proposed mention is made of those of Earp by precipitation with chrome alum or lead acetate; of Parker and Casaburi by precipitation with ferric chloride, the final estimation in both cases being made by nitrogen determination (Kjeldahl). Kopecky (*Collegium*, 1907, 241) emphasizes the necessity of a rapid process for practical control and titrates the soaks before and after use, the difference representing the bases from fermentation. Author objects to this that the first products of fermentation are acid and only later become basic. His proposed method depends upon a reaction observed by Schiff that amino-acids by condensation with formaldehyde are increased in acid character.




(inner salt)

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There are many representatives of the amino-acids in soak and lime liquors formed by hydrolysis of the albumenoids of the hide; according to the extent of this, albumoses, peptones, amino-acids and finally ammonia itself, are formed. The analytical principle is to titrate the liquors before and after addition of formaline (this was suggested by a work of Sörensen upon peptones). This cannot be applied direct however, for sulphides are present in these liquors and react with formaldehyde, increasing the alkali; they are removed by addition of zinc sulphate in excess which also removes lime and free ammonia. It is important to convert free $NH_3$ into the sulphate for this reacts with formaldehyde giving hexamethylene tetramine and free $H_2SO_4$.

*I. Process for Soak Liquors.*—200 cc. are placed in a 250 cc. flask, 20 cc. of 5 per cent. zinc sulphate solution added and filled to mark; the whole is shaken, let stand a few minutes and filtered through a folded filter; 50 cc. of filtrate are mixed with 10 cc. of 40 per cent. formaldehyde and titrated with 1/5N. NaOH (phenolphthaleïn). The formaldehyde is either previously de-acidified with $BaCO_3$ or its acidity determined and allowed for. Another 50 cc. are likewise treated without formaldehyde addition and titrated as before to the same end color; this is less distinct than with the formaldehyde. The following analyses were obtained with a series of soak liquors.

| Soak No. | titration difference in cc. 1/5N. NaOH | | mg. N (Kjeldahl) | mgs. N to 1 cc. titr. diff. | |
|---|---|---|---|---|---|
| | a. | b. | | a. | b. |
| 1 | 2.7 | 2.5 | 18.9 | 7.0 | 7.6 |
| 2 | 2.7 | 2.6 | 20.65 | 7.6 | 7.9 |
| 3 | 5.6 | 5.8 | 40.25 | 7.2 | 6.9 |
| 4 | 5.0 | 4.6 | 36.4 | 7.3 | 7.9 |

In series (a) $Na_2S$ was intentionally added and made ineffective by addition of $ZnSO_4$, series (b) represents the unaltered soak liquor; the agreement is good. The titration difference is also seen to be proportional to the nitrogen contents.

*II. Process for Lime Liquors.*—As with soaks, using however 50 cc. zinc sulphate solution. Since the decomposition products are much more varied here than in soaks, the titration differences cannot be expected to be directly proportional to the N present, ammonia for instance having a much higher N content. If desired, ammonia may be removed before titration by the method of Procter and McCandlish (*Collegium*, [1906] 270); Arnstein (*abstr. this JOURNAL*, 1908 (3) No. 10, p. 318). In the following analyses with a series of limes, it is at least to be seen that the titration differences increase with age. It remains for the tanner to determine limits for practical control. The method is rapid and sufficiently accurate.

| No. of lime | titration difference in cc 1/5N. NaOH (100 cc. liquor) | mgs. N (Kjeldahl) | mgs. N to 1 cc. titr. diff. |
|---|---|---|---|
| 1 | 2.0 | 19.6 | 9.8 |
| 2 | 17.0 | 142.8 | 8.3 |
| 3 | 19.0 | 162.4 | 8.5 |
| 4 | 26.5 | 305.2 | 11.5 |
| 5 | 34.5 | 432.6 | 12.5 |

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**A Sensitive Colloidal Reaction for Some Metallic Salts.** E. STIASNY. *Collegium*, 1908, Nos. 325 to 6, pp. 348, 357.—If to 2 to 5 cc. of a dilute solution of an aluminum salt, 5 cc. $^1/_{10}$ per cent. tannin solution be added, followed by 10 cc. of normal sodium sulphate solution and the whole be boiled, there forms immediately a flocky precipitate, even when only .01 mg. $Al_2O_3$ per cc. be present; blank tests (without Al salt) remain clear for hours. The reaction is explained as a colloidal precipitation occasioned by electrolytes. Other salts may be used for these: sodium acetate works in the cold while the sulphate requires heating. Also salts of Ca, Ba, Sr, Mg, Zn, Pb, Cr, Fe and Mn my be substituted for Al, but only Mn approaches Al in sensitiveness. The author applies the reaction to sulphite-cellulose waste lye which is in the market in concentrated and purified state as "pine-wood extract"; this has been proposed as a tanning material and is probably used in adulterating extracts. It is doubtful if it has real tanning power, although partly absorbed by hide-powder and precipitated by gelatine. Formaldehyde gives no precipitate and the iron reaction is feeble. This extract fails to give the reaction with alum, which is held to disprove its containing genuine tans. It gives a precipitate on addition of tannin solution with electrolytes, this being due to its containing Mn and Al salts, the test being distinct when the waste lye forms as much as 10 to 20 per cent. of the mixture. Hence a failure of the test (best by boiling 5 cc. tan extract with 10 cc of 10 per cent. sod. acetate) shows that there is little adulteration with waste lye. A positive test however does not prove such adulteration since the salts occasioning the reaction may be present from other sources.

**Physical Theory of Tanning.** H. BOULANGER. *Bull. Soc. Industrielle du Nord de la France*, 1907; abstr. in *Le Halle aux Cuirs*, 1908 [52], Nos. 36-41.—The essential theme here is the microscopical examination of leather and its applications. If a section be cut from a fresh ox-hide and stained with Weigert's solution, an examination shows two distinct regions. The region in contact with the hair contains an infinity of fine fibres, passing in all directions but closely interlaced about the hair sheaths, vessels, etc.; this is called the layer of elastic fibres. These elastic fibres become less towards the center of the section and finally disappear. The second region, called the layer of "conjunctive fibres," is made up of coarse fibres that are little affected by the stain.

It is difficult to make a continuous thin section of leather including the flesh as this crumbles into powder; attention is therefore confined to the grain. For preparing leather sections, a Ranvier microtome is used. A little ribbon of about 10 mm. width is taken, and most of the flesh trimmed away leaving a thickness of 1½ to 2½ mm. at the most; this is placed in warm tallow until thoroughly impregnated (about ¼ hour) and then let chill. In the mean time a little tube of paper is prepared the size of the microtome cylinder; in this as a mould, the leather sample is cemented with melted paraffine. After cooling, the paper is removed and the cylindrical black containing the leather strip is placed in the microtome cylinder and sliced with the razor in thicknesses as desired. The slices of leather are thrown into a dish of xylol and degreased, then transferred to glass mounts

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where they are washed with absolute alcohol, and finally tinted with Weigert's solution. The excess of color is washed away with alcohol followed by xylol and the section is finally mounted in balsam.

For making horizontal sections, a metallic cylinder is adapted to the microtome with a central hole of 6 to 7 mm. diameter intended to hold circlets of leather cut out with a punch; these should fit with gentle friction but without compression.

In this way a series of sections are prepared from leathers from different animals and tannages in all variations and studied for comparison. For ordinary purposes a magnification of 80 to 100 diameters may be used. The Weigert's solution brings out the elastic fibres in relief, stained with blue; the vessels, hair sheaths, conjunctive fibres and other tissues are little affected, having a grey tint. As compared with the original skin, the elastic fibres are much broken, rarely intact. This is due to the plumping, the extent and character of which may be thus studied. The cavities are seen filled with dark masses of tannin, and at a magnification of 250 to 280 diameters, the fine particles of distributed tannin.

**Chemistry of Chrome Tanning.** E. STIASNY. *Collegium*, 1908, No. 325, pp. 337-48.—*I. Single Bath Process.*—Three views have been held regarding the basicity of the absorbed chromium salt as compared with the original bath (1) that it is more basic, (2) that it is more acid, and (3) that it remains the same, all authorities assuming that the proportions are constant during the entire process. The author however believes that the ratio varies according to the stage of the process. Denham (*Ztsch. anorg. Chem.*, 1908 [57] 361) has shown that the blue and green chromium sulphates by hydrolysis give sulphuric acid and more or less basic salts according to the dilution. These two products act upon hide in quite different ways. The crystalloidal $H_2SO_4$ penetrates rapidly and is reversibly adsorbed until equilibrium is reached. The basic component is prone to colloidal change and although still possessing some power of diffusion, it adds adsorption proceeds only gradually and is non-reversible. It is to be expected therefore that when tanning begins, much acid and less base are taken up, the las increasing with time. The basicity of the liquor therefore would increase at first and then gradually fall off. This is confirmed by the following tanning experiments made upon cubes of butt with (I) sol. of pure chromium sulphate; (II) basic salt, approx. $Cr(OH)SO_4$; (III) basic salt above, with sodium chloride added to retard the swelling of the hide which complicates the situation.

| | Ratio of $SO_4$ to 52.1 Cr. | | |
|---|---|---|---|
| | I. | II. | III. |
| Original liquor | 146.1 | 105.5 | 101.2 |
| After 15 minutes tannage | 133.3 | 100.4 | 95.2 |
| " 1 hour " | 123.3 | 101.2 | 95.8 |
| " 4 hours " | 118.2 | .... | .... |
| " 24 " " | 121.7 | 102.1 | 97.3 |
| " 48 " " | 130.3 | 102.9 | 100.8 |

Computations based upon these analyses also showed a gradual increase of basicity in the absorbed substances.

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The influence of dilution upon the basic ratio was also investigated. By the action of wool upon alum solutions, Havrez in 1872 found that with dilute solutions a more basic portion was taken up, but more acid with concentrated solutions. Georgievics confirmed this and showed that with suitable concentrations the ratio of components removed remained the same as in the original. The author obtained similar results with hide-powder.

| | Ratio of $SO_4$ to 27.1 Al. dil. alum. sulphate 0.04 per cent. | conc. alum. sulphate 1.3 per cent. |
|---|---|---|
| Original solution | 129.7 | 127.2 |
| Remaining | 154.3 | 120.2 |
| Portion absorbed | 118.1 | 274.8 |

| | Ratio of $SO_4$ to 52.1 Cr. dil. chrom. sulphate 0.037 per cent. | conc. chrom. sulphate 1.0 per cent. |
|---|---|---|
| Original solution | 125.5 | 138 |
| Remaining " | ∞ (no Cr present) | 133 |
| Portion absorbed | 58.5 | 150 |

Experiments on the influence of various salts and protecting colloids showed the basicity of absorbed constituents unaffected.

*II. Two-Bath Tannage.*—(A.) In the first bath, the butts are saturated with bichromate and acid, with final addition of salts. Experiments were here made to study the influence of electrolytes upon the absorption of bichromate. 10 gms. of hide powder with 30 cc. $^{N}/_{10}$ HCl, 50 cc. $^{1}/_{8}$N. $K_2Cr_2O_7$ in each case and in addition the various salts below, leaving stand over night.

| | | | | | | |
|---|---|---|---|---|---|---|
| 20 cc. $H_2O$ | 76.5 | per cent. | absorbed | of | $K_2Cr_2O_7$ | used |
| 20 " $^{1}/_{5}$N.NaCl | 71.5 | " | " | " | " | " |
| 20 " " " $NaNO_3$ | 70.8 | " | " | " | " | " |
| 20 " " " $NaC_2H_3O_2$ | 70.1 | " | " | " | " | " |
| 20 " " " $Na_2SO_4$ | 61.9 | " | " | " | " | " |

The lowering of absorption by the presence of salts is seen on comparison with the blank test with water alone.

A second series of tests was made showing the extraordinary increase of absorption caused by HCl. 5 gms. hide powder were treated with 50 cc. $^{1}/_{20}$ N. $K_2Cr_2O_7$ in each case, with varying amounts of HCl, making up to a total volume of 150 cc.

| | | | | | | |
|---|---|---|---|---|---|---|
| Water alone | 10.6 | per cent. | absorbed | of | $K_2Cr_2O_7$ | used |
| 40 cc. $^{1}/_{10}$N.HCl | 58.3 | " | " | " | " | " |
| 50 " " " | 61.6 | " | " | " | " | " |
| 80 " " " | 63.8 | " | " | " | " | " |

(B.) The changes taking place in the second bath are very complicated. The reducing agent commonly used, sodium thiosulphate is the only one considered here. The reduction is carried out in HCl solution, giving, not a basic chloride as might be supposed, but a basic chromium sulphate due to its greater colloidal character, as shown by the author some years ago. Well washed leather of this tannage contains only sulphate. The simplest reactions would be

$K_2Cr_2O_7 + 6HCl + 3Na_2S_2O_3 = 2KCl + 4NaCl + Na_2SO_4 + 2Cr(OH)SO_4 + 2H_2O + 3S$.

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or 1 atom S to 1 mol. $Na_2S_2O_3$. As a matter of fact much less sulphur is liberated. A series of laboratory experiments are quoted giving from 50 to 62 per cent. yield in sulphur and this can be changed by varying the conditions. Recipes are known in chrome tanning whereby no sulphur at all is precipitated. The author has endeavored to experimentally determine the proportions of bichromate, sulphuric acid and thiosulphate which permit a reduction (without sulphur separation) with minimum of thiosulphate and acid. The speed with which the thiosulphate was added was found to affect the result, less being required with slow addition; a minimum was reached at 3 drops per minute (into boiling bichromate acid solution). These results corresponded to a consumption of $3K_2Cr_2O_7$; $7H_2SO_4$; $4Na_2S_2O_3$. The products of reaction from these are believed to be most correctly expressed by

$$3K_2SO_4 + 3Na_2SO_4 + Na_2S_4O_6 + 3H_2O + Cr_6(OH)_8(SO_4)_3.$$

Tetrathionate was detected by qualitative tests and some quantitative evidence was given.

**Tanning Materials of the Forests of New Caledonia.** U. J. THUAU. *Collegium*, No. 327, pp. 376-80.—In view of the great consumption of native chestnut by the French tanners, and its possible exhaustion, the materials obtained from the French colonies are of especial interest. Two species of mangrove grow on the coast of New Caledonia, the red and the ordinary. The ordinary mangrove, *Brugniera Rhumpii*, analyses:

| | Outer bark. | Bark complete | Bark of root. | Wood of root. |
|---|---|---|---|---|
| Tannin | 2.9 | 42.6 | 5.7 | 8.8 |
| Non-tans | 1.6 | 7.6 | 2.7 | 12.0 |
| Insoluble | 82.7 | 36.5 | 73.2 | 62.6 |

The "little mangrove," *Crossostylis Multiflora*, gives:

| | Wood (large.) | Wood (small.) | Bark. | Leaves. |
|---|---|---|---|---|
| Tans | 21.0 | 1.1 | 2.5 | 0.8 |
| Non-tans | 16.7 | 6.4 | 2.8 | 21.8 |
| Insoluble | 36.0 | 80.7 | 82.8 | 55.4 |

Some other analyses are:

| | Minea bark. | Acacia bark. | Iron wood bark. Outer. | Iron wood bark. Inner. | Guaiac bark. | Oak-gum bark. |
|---|---|---|---|---|---|---|
| Tans | 23.6 | 12.8 | 1.4 | 9.6 | 16.7 | 17.4 |
| Non-tans | 10.0 | 6.3 | 1.4 | 5.3 | 10.4 | 3.8 |
| Insoluble | 55.3 | 69.0 | 86.2 | 74.2 | 63.0 | 67.4 |

The "minea" is found in the same districts as the mangrove. The acacia grows in the highlands. The guaiac is also a mimosa (*acacia spirabilis*). The so-called "iron-wood" *Cosuarina*, is found in several species. The oak-gum, *Spermolepsis gummifera*, belongs to the *myrtaceae*. It exudes a resinous gum which, after drying, contains 79.73 per cent. gallo-tannic acid, 19.5 tanno-resin, which itself contains 47.2 per cent. tans.

**Myrabolams in Extract Manufacture.** J. WLADIKA. *Gerber*, 1908 [34], Nos. 817-18, pp. 250-51, 265.—This substance, because of its cheapness compared with domestic tanning materials, is now much used by the tanner.

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Also the extract maker finds it useful in blending his extracts; he does not however employ it as a cheapener, for mangrove is a better substitute for this purpose, containing 35 per cent. extractable tans, giving clear liquors, hot or cold. The dark-red, approaching violet color of mangrove, is however objectionable; a practiced eye is able to detect 20 per cent. of this admixture. An addition of 5-10 per cent. of the light-colored myrabolams is sufficient to mask the color of 20-25 per cent. mangrove. (It is said that a factory process is known for decolorizing quebracho mangrove mixtures enabling the manufacturer to dispense with myrabolams). It is not desirable to use more myrabolams than sufficient for this purpose since it renders leather brittle; moreover since its non-tans amount to one-half the tans and these, as shown later, deteriorate, the value of the extract is lowered by increasing myrabolams. It was formerly thought that myrabolams liquor or mixture with hot, unsettled quebracho liquors had a solvent action on the sediment, but varied and numerous experiments have shown this to be a delusion, and that the more concentrated the liquors, the greater the sediment.

In the usual preparation of liquors by leaching in closed copper diffusion apparatus as in open vats, it is of advantage to finely divide the crude material. With myrabolams however this does not pay; the fruit shell (63 per cent.) contains most of the tan and is soon softened by water, yielding up 90 per cent. of its tans at 90° before boiling is reached. The kernel is hard, resists grinding and contains at the most 25 per cent. tan-stuffs besides a peculiar oil; it has been worked up separately, especially in tanneries, but the cost of grinding hardly repays, and stoppages of the extraction apparatus make trouble. The tans of myrabolams are quite easily soluble, and 2 or at the most, 2½ parts of water are enough to give a 6° B. liquor without undue heating. Although the tans and the color suffer little by heat, it is best not to exceed 75° since 95-97 per cent. of the tans are dissolved. Increased heat and more water only dissolve non-tans. and give impure extracts. The liquor thus obtained is allowed to settle but a short time in a reservoir, to remove mechanical impurities. The usual practice in extract making of letting cool to 25° for settling is not desirable with myrabolams for on standing, like valonea, it has the undesirable property of giving much sediment, even with weak liquors; neither does the liquor after settling finally become clear, like oak-wood extract; it is found to have lost tans, due to a decomposition of the myrabolams tan-stuff into insoluble ellagic acid, gallic acid and sugars. The approximate loss may then be 15-20 per cent. of the total tans, and even more with weaker liquors which are however seldom used in practice. This decomposition of myrabolams leached liquor is more likely to occur under the conditions prevailing in tanneries than in extract factories. In the tanneries mixtures are often extracted and sediments obtained during a slow cooling when myrabolams is present; the rational process is to extract this separately.

The hot liquors to be worked for myrabolams extract, after being slightly settled, is concentrated in single or double, rarely in triple effects. Previous decolorization is unnecessary and also unadvisable for the chemicals used

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would occasion a continuous sedimentation and loss. Myrabolams extract has a limited demand; it has at the most, 27 per cent. tans and containing large amounts of non-tans is not so suitable as liquors directly prepared from the raw material.

If the myrabolams liquor is to be used for blending quebracho extract, it is mixed hot with the hot unsettled quebracho mangrove liquors and settled according to wish, and then concentrated in the vacuum apparatus.

Myrabolams can be recognized with certainty in blended extracts by Stiasny's formaldehyde reaction (*Gerber*, Nos. 740-43), which the author has repeatedly used with success. By practicing on mixtures with known varying amounts of myrabolams, one can in time make an approximate quantitative estimation.

**A Study of Tanning Extracts** (continued). U. G. THUAU. *Le Cuir*, 1908, (1) Nos. 5, 7, 9; pp. 12, 7, 19.—In 1897 Dr. Lorenzo Dufour made use of the principle of osmosis to free his sulphited extracts from sulphurous compounds. To eliminate the free or combined sulphurous acid, organic or mineral acids were added, and the freed $SO_2$ driven off by evaporation, generally in vacuo. The salts remaining were removed by passing the extracts through an osmotic apparatus.

According to Dr. George Klenk (1901), sulphited extracts after evaporation become alkaline and leather tanned with them after time takes a deeper tint (experience shows this to be rare). Furthermore, the alkaline extract was held to react with the acid liquors of tannage, becoming neutralized and giving precipitates. His process was to treat the tannin solutions simultaneously with bisulphite of soda and sulphate of alumina, the products being aluminum hydrate, sodium sulphate and $SO_2$; the alumina clarifies and decolorizes the solution. 5,000 liters of a liquor of 4° B. require 4 kg. alum sulphate and 15-20 kg. bisulphite of 38-40° B. Quebracho extracts after this procedure have 45-6 per cent. tannin for 25° B. The degree of solubility of these extracts depends upon the extent of cooling; on cooling to 20°-25°, there is a considerable separation and lowering of yield. Dr. Klenk therefore modified his process, adding the alum first and the bisulphite later. For instance 5,000 liters of the tan liquor of 6° B. are treated first with 4 kg. alum sulphate and then 40-45 kg. bisulphite. No cooling is necessary if the extracts are heated about one hour at 120°-130° (under pressure). If 150-200 kg. bisulphite are used (38°-40° B.), the heating is at 60°-80°, giving a cold soluble extract.

Summing up, all extract makers manufacture sulphited extracts; if these are well made and decolorized, they produce leather of good color. It need no longer be said as at first that they leave free sulphuric acid in the leather, rendering it brittle.

In applying mixed extracts, the tanner sometimes meets with difficulties. In one case a tannery employed sulphited extracts of quebracho and chestnut finishing with myrabolams in the drum. The entire manufacture was according to modern methods, and gave a supple leather which curried well. Later, however, the consumers complained that the grain became brittle and the leather cracked. On examination the leather was found to contain sul-

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phuric acid, but the extracts, although strongly sulphited, showed neither sulphuric nor sulphurous acids. The vat liquors on examination showed a high content in acid and also contained sulphuric and sulphurous acids. The explanation was this : the final tannage had been completed with a concentrated liquor of myrabolams alone in the drum to give good color and weight ; this had been used in excess to secure maximum gain and the residual liquor was then added to the first vats. Myrabolams extract is very unstable, its tannins under action of the air changing to gallic and ellagic acids which in this case liberated sulphurous acid for which the extract makers were not to blame. The following analysis shows the change taking place with time in myrabolams liquor of 2°B.

| | New | after 30 days |
|---|---|---|
| Tannin | 2.29 | 1.75 |
| Non-tannin | 0.98 | 0.58 |
| Insoluble | 0.5 | 0.98 |

The combination between tannin and sod. bisulphite is complicated and not understood since we do not know the constitution of tannin itself. What is of practical interest to the manufacturer and the tanner is an exact knowledge of the contents of sulphurous and sulphuric acid free and fixed ; this may be used in comparing extracts made of the same material but does not apply to those of different materials. The sulphites of soda while they lessen the intensity of the colors of extracts, impart themselves a special color. Yellow is given to the tannins of myrabolams, gambier and algarobilla, rose to valonia, rose red to chestnut, quebracho and hemlock, red to oak.

**The Liming Process. The Modern Tanner.** *Le Cuir*, 1908 (1), Nos. 5, 7, 9, 11, pp. 1-3, 1-3, 1-3, 1-3.—The object of liming is two-fold ; first to dissolve the pilline which cover the roots of the hairs where they are imbedded in the skin permitting them to be afterwards easily withdrawn mechanically; secondly to remove the fatty substances which prevent later the penetration of the tannin solution and do not contribute to leather formation. The action here is to form a lime soap which is removed in the later treatment. If these two operations are not pushed to completion, the grain of the leather will suffer from the undue force used in extracting the hair and secondly the tannage will be unsatisfactory ; the portions where the fatty material has remained will often be not half-tanned and have an undesirable dirty-gray color, also the fat acts upon the tannin, producing spots.

According to the ancient process, it was thought necessary to leave the hides a long time in the limes. They were first placed in an old lime supercharged with ammoniacal decomposition products for the hide, then in a mixed liquor and finally in fresh lime. This was erroneous; the protracted action of these liquors, particularly those charged with ammonia injured the leather and above all, dissolved hide, lowering the gain. The action of fresh and old limes upon hide are quite different. A fresh solution of calcium hydrate acts upon the roots of the hair as well as upon the epidermis; this action is however comparatively mild and depilation can only be accomplished after a great length of time. In old limes, there is less caustic

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lime, as this has been in part neutralized by organic acids and especially, there are present bacteria or microbes which multiply most rapidly in old limes, since fresh caustic acts as an antiseptic. The action of these organisms on the hide is destructive consuming it as food and producing ammonia as a by-product which is also destructive. The envelope of the hair roots is however the most rapidly attacked, hence it is important to leave the hides in old limes no longer than just sufficient to loosen the hair; after that comes loss of hide.

A quite different action of caustic lime is often not utilized as it should be, namely, the swelling of the hide substance itself. It is of advantage with many sorts of hides after loosening the hair in old limes, to afterwards treat with fresh lime to bring about this swelling. The following bate should not be such as to again contract the fibre but an acid bate which even increases the swelling. The hides are then free from lime and in condition for tanning. This method of swelling is especially suited for saddlers' leather; English tanners give the hides a prolonged swelling in fresh lime after dehairing.

To accelerate depilation in the limes mechanical agitation has been employed with success; the action is also more uniform. A simple and very efficient device for this purpose is the suspension frame. Each hide is attached to a separate bar of iron, the two ends of which rest upon the opposite sides of an iron frame, which is the same size as the vat. One side of the frame is attached to the wall of the vat forming an axis, while the opposite side is lifted up and down by a chain operated by an eccentric or other suitable mechanism. Notches in the frame keep the bars of iron the proper distance apart that the hides may not stick together. The rocking motion gives a good circulation.

Finally, in recent times liming has been carried out advantageously in rotating drums similar to those used in tanning or stuffing.

The use of sodium sulphide in depilation has all the advantages of the lime treatment and overcomes the evils arising from too lengthy a soaking in old limes. The sulphide is very soluble and can be employed in any concentration desired and is not altered by the air. Its solution attacks the hair sheaths and the horny covering of the grain, and later the hair itself. In solution, it becomes hydrolyzed into sulphydrate and free alkali and this last saponifies the fats, hinders the growth of bacteria and also swells the hide, but more rapidly than lime. Sodium sulphide is however not generally employed by itself but mixed with lime. In this case, sulphydrate of lime is produced which is even more active in depilation than the sodium compound. Experience shows that the use of sulphide shortens the time of liming and increases gain.

**Dehairing with Sulphurous Acid.** U. G. THUAU. *Collegium*, 1908, No. 326, pp. 362-6.—An account is given of some studies made upon this process in the interests of the inventor, E. LeConte. Salted hides are placed directly without pre-soaking in a weak solution of sulphurous acid, the strength of which is maintained for 8 days when the hides may be dehaired and rinsed and are then ready for tannage. The action differs from that of

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lime or sulphides; with lime, the pilline enveloping the roots of the hair, and the Malpighian layer are destroyed and the hair itself is somewhat damaged; sulphides attack the hair and the pilline remains intact. With sulphurous acid the pilline only is destroyed and the hair comes off in masses together with the thin skin overlying the grain. Non-salted hides swell exceedingly, gelatinizing in strong solutions, without depilation. Salt is necessary which forms sulphite of soda which is considered the real agent. Experiments showed that if the salted hides were placed in a weak bath of acid which was gradually strengthened, the depilation was poor. The best results are obtained with re-salted hides placed immediately in a bath sufficiently strong in $SO_2$ (0.3° B.) In a North France tannery the yield in white weight was the same for $SO_2$ as with lime. On tanning the absorption of tannin was much more rapid than with the limed hides. The new process if perfected and successful will have the advantage of doing away with soaking, and being antiseptic, there will be no offensive and unsanitary fermentation.

**Frauds in Crude Hides.** A. SCHMIDT (continued). *Le Cuir*, 1908 (1), Nos. 5,7,9. pp. 8-10, 8-9, 3-5.—The first method of valuing salted hides as previously outlined (This *JOURNAL*, 1908 (3)No.9. p. 284), namely by taking the weight of the salted hides directly as received is practised largely in Germany. By practice, controlled by salting experiments on fresh hides, the expert can judge with accuracy by the appearance of the hide, its relative weight when fresh, the loss by salting being from 6 to 20 per cent. according to dryness. The hide is suspended, beaten on the flesh side to shake off salt and then inspected and a factor assigned according to appearance. Very moist hides are given a coefficient of 94 to 92 per cent., that is, the weight of the salted hide divided by 0.92 = weight of fresh hide (by which it is sold). For 92 to 90 per cent., the hides still appear moist and are likewise insufficiently salted. When the flesh side appears moist in places, about ⅓ total surface, the remainder being firm but not dry and the hair side normally moist, 90 to 88 per cent. are assigned. 88 to 86 per cent. is given to the normal condition of a well-salted hide; the flesh is firm throughout, showing, no glistening moist spots, also no spots hardened by salt; the hair side is neither dry nor moist. When the flesh is partly hardened by salt upon $^1/_5$ the surface, the factor is 86 to 84 per cent. When the hard portions amount to ⅓, having a brown appearance, 84 to 82 per cent. is the rate. Finally with badly treated hides, such as those exposed to the sun or a current of air, the flesh being entirely brown and hardened by salt, the factor is 82 to 80 per cent.; this case is rare. In addition, hides of very open structure (from bulls and young cattle); the above losses should be increased by 1 per cent.; with extremely dense hides, such as from old cows, the loss is 1 per cent. less.

The second method of control consists in comparing the weight of the hides after soaking with the fresh weight given by the seller; the ratio should be 103 to 105 per cent. This method much used may be practiced in several ways; (1) the horns and tail are left on the hide and not removed until after soaking and weighing, the normal ratio being 103 to 105 per cent.;

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(2) the horns and tail are removed before soaking and not counted, the normal rendement being 98 to 100 per cent.; (3) the horns and tail are removed as above, weighed, and this weight added to that of the softened hides, the result being the same as in (1). If these results are all duly registered, the tanner by aid of his books can detect deficits in crude material. A model sample is given of such a register from which we cite the headings of the columns

| Date. | Dealer. | Fresh weight. (dealer). | Weight after soaking hide. | horns and tail. | total. | Rende- ment. | Temp- erature. | Remarks. |
|---|---|---|---|---|---|---|---|---|

In applying the control, it is of course necessary that the tanner always operate according to a uniform process. The salted hides are best suspended in the soaks without being in contact, remaining in fresh water 24 hours, being lifted several times meanwhile; they then drain 12 hours on a horse and are weighed. The duration of soaking has a great influence upon the results; when prolonged, more water is taken up and permanently retained. Moreover, protracted soaking brings about fermentation which causes loss of hide and lowers gain. Temperature has also great influence; although the reason is not fully understood, it is well known that hides swell more in cold water than in warm. The following rendements were obtained (reckoned against fresh hide) at different temperatures, all other conditions being strictly the same.

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Soaking | in | water | at | 1°C | gave | 109.0 | per | cent. |
| " | " | " | " | 4 | " | 107.0 | " | " |
| " | " | " | " | 7 | " | 106.0 | " | " |
| " | " | " | " | 10 | " | 105.0 | " | " |
| " | " | " | " | 13 | " | 104.25 | " | " |
| " | " | " | " | 16 | " | 103.5 | " | " |
| " | " | " | " | 19 | " | 102.5 | " | " |
| " | " | " | " | 22 | " | 100.75 | " | " |

It is best therefore in order to get a reliable control to soak at a uniform temperature (10-15°), summer or winter, heating the liquor by steam in cold weather; a regular manufacture is also attained.

Minor factors influencing the yield after soaking are length of hair (the absorption of water being less with short hair), the age of the animal and the effect of putrefaction resulting from imperfect salting; these must be judged by the tanner.

**Treatment of Pickled Splits.** *Ledermarkt.*, 1908 [30], No. 73, p. 10.—*Query:*—How should pickled splits be delimed? *Ans.*—If they require deliming the splits were not really pickled; they should contain no trace of lime. If properly pickled, they should appear perfectly white and opaque. To prepare for tannage, they are thrown into a drum containing cold soft water to which 5 to 7 per cent. of slimed chalk has been added. The hides are milled 20 to 30 minutes, the liquid then run off and replaced by fresh water, and the whole milled again ½ hour. This depickling restores the ware to

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the condition of crude butts, and it has the familiar gelatinous appearance. It is important that the stock so long as it is pickled does not come in contact with clear water, as it will swell and be unfit for tanning.

**Stain for Alum Tanned Leather.** *Le Cuir.*, 1908 (1), No. 9, p. 22.—There is considerable demand for a permanent red color in this leather. Aniline dyes are generally the most brilliant but are affected by light and air, therefore vegetable dyes are employed, particularly Brazil wood. The finely dried material is sprinkled with lukewarm water, exposed to the light for 6 hours and then placed in a vessel of warm water and boiled gently until evaporated one-half, the wood still being covered. The solution is then filtered through cloth and to this while still hot, 77 centigrams alum added per kilo of wood. The leather is mordanted with a second boiling from the wood slightly acidulated with sulphuric acid and applied with a brush. After this has penetrated the leather, the first extract is also applied taking care to spread the tint uniformly. Two coats are generally sufficient and the hides are then rinsed with a dilute solution of alum made acid with some organic acid. Water freed from lime is required for this work.

**Currying Chrome Leather for Pneumatics.** *Gerber-Zeitung.*, 1908 [51]-No. 202.—The dry leather is treated with a solution composed of 85 parts benzine, 10 parts benzol, 3 parts naphtha and 5 parts kreosine remaining there 30 minutes. The leather is then spread on a table flesh upward and the solution rubbed out with a brush. This is repeated several times and the leather dried again and then treated with a solution of 20 parts Para caoutchouc and 1 part fish gelatine in 80 parts benzine, 10 parts benzol and 2 parts naphtha.; the caoutchouc is dissolved first in the benzine, the other solvents added and last of all the gelatine previously dissolved in a little water. This solution is divided into three parts. The first one is used unchanged, the second is diluted with 10 parts benzine and $\frac{1}{8}$ part naphtha and the third is diluted with double these amounts. The leather is treated with these three solutions successively, remaining in the first 4 hours, in the second 7 days and in the last four days, when it is rubbed with the brush and hung up to dry. Then follows another treatment with a solution of 5 parts kreosine, 1 part naphtha, 25 parts benzine and 20 parts benzol. The leather is finally stretched and dried.

**Waterproof Sole Preservative.** *Gerber-Zeitung.*, 1908 [51], No. 202.—10 parts paraffine are melted with 10 parts of linseed oil and to this 2 parts spirits of turpentine are added. The mixture is applied warm to the soles or the leather is frequently dipped therein. After cooling, the excess is scraped off.

**A Brilliant Dressing for Box Calf.** *Le Cuir*, 1908 (1), No. 10, p. 25.—1 litre blood, 1 litre logwood decoction, whites of 4 eggs, 36 gms. alcohol, ½ litre milk, 15 gms. powdered galls, 1 litre water.

**Sizing for the Flesh of Gloss Leather** (same).—1 kg. Iceland moss is boiled with about 20 litres of water to a pasty mass, adding a little traga-

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cauth, starch and talc. The more talc and starch taken, the whiter the flesh. To improve the unnatural hue a yellow color is added, or a solution of cutch. The size should not be applied in too thick layers, but best in two coats.

**Chrome Black for Small Chromed Skins** (same).—This is a violet black applied in the same fashion as sulphate of iron. After the skins have been wheeled 30 min. in logwood solution, a solution of 12 gms. per litre of bichromate of potash is added, leaving run 15 minutes more and thoroughly washing.

**Commercial Sicilian Sumac.** F. P. VEITCH. *U. S. Dept. of Agriculture, Bureau of Chemistry, Bulletin* No. 117. (Including notes on the microscopical detection of adulterants by B. J. Howard). The analyses of several hundred samples of commercial Sicilian sumac are tabulated, with notes on the interpretation of the results obtained. Methods for making microscopical examinations of the samples are also described, and some helpful illustrations accompany these methods.

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## PATENTS.

**Apparatus for Stretching Leather Hides, or Skins, U. S. Patent No. 901,324.** A. CLEVELAND, Newark, N. J.

**Tanning Ooze, U. S. Patent No. 901,564.** G. A. SWEETMAN, Bickford, Oklahoma. A tanning bath consisting of soft water, ten gallons; Bengal catechu, one-fourth pound; septfoil root, three pounds; aleppo galls, one-half pound; ground hops, one-fourth pound; and powdered gum senegal, one-fourth ounce.

**Process for Bleaching Fats, Oils, etc. U. S. Patent No. 901,718.** K. LUDECKE, Charlottenburg, Germany.—A process of bleaching fats, fatty oils, mineral oils, resins, waxes, paraffin, yolk, fatty acids and the like which consists in dissolving, without aqueous solutions, organic superoxids in the material to be bleached, avoiding emulsions and heating the solution.

**Cactus Leather. U. S. Patent No. 902,359.** F. C. WRIGHT, Tucson, Arizona.—A process of producing imitation leather from cactus, consisting in cutting the cactus plant into sections of the desired size and thickness, immersing such sections in a tanning bath or solution until cured, removing the sections from the bath and drying.

**Method of Treating Hides, U. S. Patent No. 903,034.** W. J. WARD, Philadelphia, Pa.—A method of treating hides, preparatory to tanning the same, which consists in subjecting the hides to the action of a liquid containing the result of the reaction of 84 pounds of water to 20 pounds of lime, and 10/16 of a pound of sulfate of iron before the reaction has proceeded to its ultimate stage.

**Leather Finishing Machine, U. S. Patent No. 903,181.** A. E. DODGE, Lynn. Mass.

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**Spring-Roll for Leather Splitting Machines, U. S. Patent No. 903,559,** J. H. GAY AND W. D. QUIGLEY, Newark, N. J.

**Machine for Treating Hides or Skins, U. S. Patent No. 904,079.** D. P. O'BRIEN, Woburn, Mass.

**Leather Working Machine, U. S. Patent No. 904,160.** W. H. STIMPSON AND F. A. BRADFORD, Dorchester, Mass.

**Machine for Rounding Leather, U. S. Patent No. 904,445.** R. A. PFEIFER, Austin, Texas.

**Process of Decolorizing Tannin Extracts, U. S. Patent No. 904,483.** A. HUGENDUBEL, Stuttgart-Feuerbach, Germany. The process of decolorizing tannin extracts which consists in treating the same with chromous compounds derived from chromous protoxid (CrO).

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